PB 198 427

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

BLANK PAGE

1 Accession Number

W71-07052

2 Subject Field & Group

05D,05G

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

5 Organization

Tyco Laboratories, Inc, Waltham, Massachusetts,

6 Title

SILICATE TREATMENT FOR ACID MAINE DRAINAGE PREVENTION, Silicate and Alumina/Silica Gel Treatment of Coal Refuse for the Prevention of Acid Mine Drainage,

10 Authors

16 Project Designation

EPA-WQO Contract No.: 14-12-560

21 Note

EP 2,10:14010 DLI 02/71

Copy available from GPO Sup Doc as , $1.00 ; microfiche from NTIS as PB198 427, $0.95.

22 Citation

EPA-WQO Report 14010DLI, February, 1971, 94p, 17 fig, 31 tab, 10 ref, 3 append,

23 Descriptors (Starred First)

Wastewater treatment, *Silica, *Gels, Mine drainage, ~~*Coal refuse~~ Water pollution control, Weathering, Neutralization, *Acid mien water,

25 Identifiers (Starred First)

*Coal refuse, *Alumina/silica gel, Waterglass,

27 Abstract

A treatment technique has been demonstrated on a laboratory scale which inhibits or prevents the generation of acid mine water from waste coal refuse. Three variations of the general method were considered:

1. Neutralization of the water-accessible refuse with a dilute solution of sodium silicate (waterglass)
2. Development of a continuous gel on the refuse surface structure which sealed off the entire pile from natural runoff waters
3. Development within the pile structure of a continuous silica/aluminia gel to eliminate percolation through the refuse and minimize the effect of natural erosion of the gel structure.

Comparison of the effluent water with an untreated pile shows that the neutralized pile was effective for a minimum of 120 in. of equivalent rainfall in inhibiting AMD generation. The surface gel was effective for a longer period of time. The most effective treatment utilized a mixed alumina/silica gel formed within the pile at depths up to 6 in. This method was effective for more than 500 in. of equivalent rainfall, the duration of the test, and appeared to be exceptionally stable at that time.

The weathering resistance of the treatment methods was evaluated by heating the gel treated refuse in the laboratory and exposing it to rain, snow, and freeze-thaw cycles outdoors. Extensive washings of the weathered test materials established the fact that the treatments were effective for at least 120 in. of equivalent rainfall (the duration of the test) in preventing AMD generation.

Abstracto

:R

WR:102
WRSIC

[illegible] D 0SG.

6) Silicate Treatment For Acid Mine Drainage Prevention,

(12) [illegible]

Silicate and Alumina/Silica Gel Treatment of Coal Refuse for the Prevention of Acid Mine Drainage,

final [illegible]

~~by~~

5) Tyco Laboratories, Inc,
~~Bear Hill~~
Waltham, Massachusetts. ~~02154~~

for the

ENVIRONMENTAL PROTECTION AGENCY
WATER QUALITY OFFICE

~~Project No.: 14010DLI~~
16) EPA-WQO Contract No.: 14-12-560

22) EPA-WQO Report 14010DLI, February, 1971, 94p, 17 fig, 31 tab, 10 ref, 3 append

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $1

1) (Contributor stamp)

(23 + 25 [illegible] [illegible])

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

27) A treatment technique has been demonstrated on a laboratory scale which inhibits or prevents the generation of acid mine water from waste coal refuse. Three variations of the general method were considered:

1. Neutralization of the water-accessible refuse with a dilute solution of sodium silicate (waterglass)

2. Development of a continuous gel on the refuse surface structure which sealed off the entire pile from natural runoff waters

3. Development within the pile structure of a continuous silica/aluminia gel to eliminate percolation through the refuse and minimize the effect of natural erosion of the gel structure.

Comparison of the effluent water with an untreated pile shows that the neutralized pile was effective for a minimum of 120 in. of equivalent rainfall in inhibiting AMD generation. The surface gel was effective for a longer period of time. The most effective treatment utilized a mixed alumina/silica gel formed within the pile at depths up to 6 in. This method was effective for more than 500 in. of equivalent rainfall, the duration of the test, and appeared to be exceptionally stable at that time.

The weathering resistance of the treatment methods was evaluated by heating the gel treated refuse in the laboratory and exposing it to rain, snow, and freeze-thaw cycles outdoors. Extensive washings of the weathered test materials established the fact that the treatments were effective for at least 120 in. of equivalent rainfall (the duration of the test) in preventing AMD generation.

This report was submitted in fulfillment of Contract No. 14-12-560 between the Federal Water Quality Administration and Tyco Laboratories, Inc.

KEY WORDS

23) Waste-water treatment
*Silica, *gels,
~~Acid~~*mine drainage
25)*Coal refuse
5)Alumina/silica gel
Water pollution control,
*Acid mine water

~~Accelerated testing~~
Weather~~ability~~ing
Neutralization
25)Waterglass
~~Gel forming methods~~

Table of Contents

Section No. Page No.

ABSTRACT ii

1 CONCLUSIONS 1

2 RECOMMENDATIONS FOR FUTURE WORK 3

3 INTRODUCTION 5

4 THE TYCO TREATMENT APPROACH 7

5 DETAILS OF REFUSE PILE TREATMENTS 11

6 RESULTS AND DISCUSSION 15

7 GEL WEATHERABILITY TESTS 27

8 TREATMENT OF ACID MINE DRAINAGE 33

9 OTHER EXPERIMENTS 53

10 MASS BALANCE 57

11 REFERENCES 69

12 PUBLICATIONS 71

Appendix No. Page No.

I ANALYTICAL METHODS 73

II COMPLETE ANALYSIS OF PILE EFFLUENTS 75

III AMD GENERATION MECHANISM 93

BLANK PAGE

List of Illustrations

Figure No. Page No.

1. Gel Times at 25.0 °C of 3.22 Ratio Sodium Silicate as a Function of pH 13

2. Iron Content of Wash Effluent From Four Tests Piles Compared to Control Pile. 16

3. pH of Wash Effluent From Pile B (Neutralized Pile) Compared to Pile A (Control) 17

4. pH of Wash Effluent From Pile C (Silica Gel-Surface Gel) Compared to Pile A (Control) 18

5. pH of Wash Effluent From Pile D (Alumina/ Silica Gel - Surface Gel) Compared to Pile A (Control) 19

6. pH of Wash Effluent From Pile E (Alumina/ Silica Gel-Gelled in Depth) Compared to Pile A (Control) 20

7. Rate of Iron Removal From Piles 22

8. Rate of Sulfur Removal From Piles 23

9. Determination of the Minimum Amount of Waterglass Needed to Complex Ferric Iron in Ferric Sulfate Solution 37

10. Determination of the Minimum Amount of Waterglass Needed to Complex Ferrous Iron in Ferrous Sulfate Solution. 39

11. Oxidation of Ferrous to Ferric in the Presence of Silicate 41

12. Amount of Sodium Aluminate Needed to Precipitate Ferrous Iron 43

13. Amount of Sodium Aluminate Needed to Precipitate Ferric Iron 44

List of Illustrations (Cont.)

Figure No. Page No.

14. Determination of Amount of Lime Needed to Precipitate Ferrous Iron 46

15. Determination of Amount of Lime Needed to Precipitate Ferric Iron 47

16. Comparison of Settling Rates Using Sodium Aluminate and Lime to Precipitate Ferrous Iron 50

17. Comparison of Settling Rates Using Sodium Aluminate and Lime to Precipitate Ferric Iron 51

List of Tables

Table No. Page No.

I. Analysis of Barnes and Tucker Bituminous Coal Refuse 9

II. Wash Analysis of Heated Pile 28

III. Wash Analysis of Heated Pile 29

IV. Analysis of Collected Water From Outdoor Test 31

V. Analysis of Effluent Water From Washing Refuse Used in Outdoor Test 32

VI. Treatment of Ferric Sulfate With Waterglass and Sodium Aluminate 34

VII. Treatment of Ferrous Sulfate With Waterglass and Sodium Aluminate 38

VIII. Oxidation of Ferrous to Ferric in the Presence of Silicate 40

IX. Precipitation of Ferrous Iron by Sodium Aluminate 42

X. Precipitation of Ferrous and Ferric Iron With Lime 45

XI. Iron Solution Treatments 48

XII. Settling Rates 49

XIII. Solids Content of Iron Precipitates 52

XIV. Optimization Studies for Alumina/Silica Gel Composition Showing Gel Time (sec) and Gel Consistency 53

XV. Analysis of Supernatant AMD in Gel Stability Tests 54

List of Tables (Cont.)

Table No. Page No.

XVI. Equilibrium Between Fe^{3+}, Fe^{2+}, OH^-, SO_4^{2-} 57

XVII. Log Equilibrium Constants for Fe^{3+}, Fe^{2+}, OH^-, SO_4^{2-} Species 58

XVIII. Computer Printout 60

XIX. Sample Output 63

XX. Comparison of Parameters for Standard Samples 65

XXI. Relative Amounts of Soluble Iron Species 66

XXII. Typical AMD Samples 67

XXIII. AMD Samples Corrected for Sulfate 68

XXIV. Sulfate Analysis, ppm 74

XXV. Sulfate Analysis (PPM) With and Without Preoxidation 74

XXVI. Pile: Control 75

XXVII. Pile B: Neutralized Pile 80

XXVIII. Pile C: Silica Gel (Surface Treatment) 82

XXIX. Pile D: Alumina/Silica Gel (Surface Treatment) 86

XXX. Pile E: Alumina/Silica Gel (In-Depth Treatment) 90

XXXI. Rapid Washing of Coal Refuse 94

SECTION 1

CONCLUSIONS

The following conclusions are based on the experimental work accomplished during this program:

1. Neutralization of coal mine refuse by treatment with waterglass (sodium silicate)is an effective technique for preventing or minimizing acid mine drainage (AMD) generation for a period in excess of 120 in. of equivalent rainfall.

2. Sealing the coal mine refuse pile surface to water percolation with silicate-based gels is effective in preventing or minimizing AMD generation over a long period, perhaps in excess of 400 in. of equivalent rainfall.

3. Alumina/silica gels are more effective in prolonged sealing of the refuse structure than are the silica gels because of the lower water solubility of the alumina/silica gel structures.

4. Surface gels are not stable to extremes in temperature. Both heating and freezing cause coagulation of the gel with the resultant loss in continuity. Such broken gels no longer seal the refuse structure, but the residual effects of the treatment minimize the generation of AMD over prolonged periods of time, similar to the effect of neutralizing the material with silicate.

5. In depth gelation of refuse piles using alumina/silica gels should be effective in prolonged prevention or retardation of AMD generation regardless of the environmental temperature variations.

6. The treatment of AMD water with sodium silicate and sodium aluminate in a holding pond is no more effective than the conventional application of lime. There is no advantage in settling rates or precipitate volume.

SECTION 2

RECOMMENDATIONS FOR FUTURE WORK

The viability of using sodium silicate gels with and without sodium aluminate to inhibit or prevent AMD generation from waste coal refuse has been successfully demonstrated in the laboratory. It is therefore recommended that the following work be continued to demonstrate the effectiveness (including cost effectiveness) of the treatment procedure:

1. Laboratory optimization of the treatment procedure for cost, depth of gelation control, quantity of chemicals, and demonstration of means of field application

2. Selection of several conditions for field evaulation under carefully chosen conditions to assess and compare percolation and run-off, and duration of effectiveness

3. Field evaluation over a 2-yr period, followed by determination of effectiveness of overplanting

4. Comparison of field results with laboratory data to provide a correlation of results for future utilization of method.

SECTION 3

INTRODUCTION

THE ACID DRAINAGE PROBLEM

The discharge of acid mine drainage (AMD) into streams of Appalachia may qualify as the single most significant pollution problem present today by virtue of the severity of damage to the streams and the effort that will be required to overcome this problem.[1] In Pennsylvania alone, the quantity of AMD produced is approximately 1.5×10^9 gal/day.[1] The magnitude of continuing treatment cost to eliminate AMD contamination from Pennsylvania's stream system has been estimated to be in excess of one hundred million dollars per year after an outlay of several hundred million dollars for treatment facilities.[1]

All methods of coal mining, whether surface or underground, contribute to this undesirable phenomenon. The refuse materials from coal mines and coal cleaning are major sources of AMD, since the breaking and crushing operations necessary for mining and coal separation provide a tremendous increase in particulate surface area available for oxidation. In the anthracite region of Pennsylvania alone, there are 270 culm and silt banks estimated to contain seven-hundred and fifty million tons of refuse.[2] Approximately four times this much material exists in the bituminous regions of the state.[2]

Extensive work is underway to develop and demonstrate methods for either preventing the formation of AMD or treating it before its seepage into streams. Prevention is far to be preferred, because it would hopefully offer a final solution to the problem rather than require a continuing and perhaps growing treatment cost. Methods considered for prevention include diversion of the surface drainage, elimination of air, passivation of the rock surfaces, deactivation of bacteria associated with AMD formation, cultivation of s
fate-reducing bacteria (within the rock strata) to reverse the action of t
sulfate-forming bacteria, and modification of pH (within the rock strata) above that conducive to AMD formation.

Under the subject contract, Tyco Laboratories has been engaged in developing a method which will prevent the generation of AMD by direct treatment of the coal mine refuse. The basis of the method, which has been shown to be feasible on a laboratory scale, is to isolate the AMD generating sites from drain water via treatment of the coal refuse with a solution of sodium silicate or sodium silicate plus sodium aluminate.

BACKGROUND CHEMISTRY: FORMATION OF ACID MINE WATER

Waste coal refuse containing significant amounts of pyrite will, in the presence of air and water, generate a dilute solution of iron sulfate and sulfuric acid. Secondary reactions between these ingredients and the local minerals will add concentrations of aluminum, manganese, calcium, magnesium, and sodium to the effluent water.

The overall stoichiometry for the acid generation process is:

$$4\ FeS_2 + 15\ O_2 + 14\ H_2O \rightarrow 4\ Fe(OH)_3 + 8\ H_2SO_4 \qquad (1)$$

The mechanism of this reaction is under study; there is some evidence that microorganisms also contribute to pyrite oxidation.[3,4,5]

This reaction proceeds in stages, the first involving the formation of soluble ferrous sulfate:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ FeSO_4 + 2\ H_2SO_4 \qquad (2)$$

Air will then slowly oxidize ferrous iron to ferric:

$$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O \qquad (3)$$

which, as the acid becomes more dilute and/or the soluble iron content increases, will hydrolyze:

$$Fe_2(SO_4)_3 + 6\ H_2O \rightarrow 2\ Fe(OH)_3 + 3\ H_2SO_4 \qquad (4)$$

The quantity of these pollutants in acid mine water is variable, and depends on the particular pyrite-coal source and the history of the water before reaching the analyst. The worst cases have a pH less than 2.5 and soluble iron contents up to 10,000 ppm.[6]

SECTION 4

THE TYCO TREATMENT APPROACH

MECHANISMS

To prevent the generation of acid mine water, it is necessary to interrupt reaction (1) at some point. Tyco's approach has been to prevent access of the pyrite to water via the formation of a silica gel over the potentially active acid generation sites. This treatment is based on the following reaction:

$$Na_2SiO_3 + H_2SO_4 \rightarrow (SiO_2)_n + Na_2SO_4 + H_2O \qquad (5)$$

When a solution of sodium silicate (waterglass) is neutralized below pH 10.7, silicic acid is first formed:

$$SiO_3^{2-} + 2\,H^+ \rightarrow H_2SiO_3 \qquad (6)$$

Initially, silicic acid and metasilicic acid (Eq. 6) are monomeric. On aging, a three-dimensional structure of Si-O-Si bonds is formed and the solution sets into a gel. The rates at which these reactions take place depend, in a complex fashion, on pH, temperature, and sodium silicate concentration.

A second set of reactions can also be involved, i.e., the precipitation of iron silicate. According to the literature,[7] most transition metal silicates, including both ferrous and ferric silicate, are extremely insoluble, forming the basic chemical structure of most rock formations. A solution of a soluble silicate, in which the anions exist as monomers, dimers, and possibly trimers, reacts rapidly to form insoluble precipitates. The extent to which this takes plate is a function of pH and the oxidation state of the iron. Ferrous silicate is apparently more insoluble than ferric silicate (see data in Section 5). At high pH, e.g., ~ 10, soluble complex ions are also formed. However, under the conditions of AMD generation, i.e., at low pH, the addition of sodium silicate can result in the formation of some insoluble iron silicate mixed in with the gel developed according to reaction (5).

Thus, there are three mechanisms by which treatment of coal mine refuse will silicate can inhibit the generation of acid mine water:

1. Blocking AMD generation with a water impermeable silica gel

2. Precipitation of iron silicate which (a) scavenges soluble iron and (b) also coats the pyrite particles

3. Neutralization of AMD acid, as per reaction (5).

Our experiments have indicated that all three mechanisms are operative. When a surface gel is formed, most water is diverted from the pile. On disrupting the gel, the effluent water composition becomes similar to that from the neutralized pile. Insoluble iron silicate is observed on removing samples of refuse from inside the pile.

EXPERIMENTAL METHODS

Treatment techniques were evaulated by testing piles of actual coal mine refuse under simulated natural conditions. The test piles each consisted of 200 kg of representative refuse, formed to a cone 3 ft in base diameter and 18 in. high. A measured artificial rainfall (generally 100 liters/day which is about 6 in. of water) was maintained on essentially an 8-hr per day, 5-day work schedule, with percolated and runoff water samples being collected on a daily basis. The wash water samples were analyzed for total iron, ferrous iron, sulfate, pH, calcium carbonate acidity, and soluble silica (see Appendix I).

The test piles were placed in plastic basins on a tilted table to allow easy collection of the runoff. An overhead sprinkling system was constructed to simulate intermittent rainfall. The plastic basins had two sample points from which the runoff and percolated wash water were collected: one collecting from a 14-in.-diameter center area and the other from the outer annulus. The data reported are for composite samples of the two collection points.

The specific refuse material used for evaluation was a washed waste coal refuse originating from the lower Kittanning Seam. The analysis is given in Table I.

Table I. Analysis of Barnes and Tucker Bituminous Coal Refuse

Size Passed	Retained	Wt %	% Pyritic Sulfur (Dry Basis)	% Fe_2O_3 (Ignited Basis)	% Sulfur*	% Ash*	% Moisture*
	1/2 in.	2.5	4.14	14.53	5.41	2.82	0.98
1/2 in.	3/8 in.	10.5	3.12	11.45	3.62	54.11	1.01
3/8 in.	1/4 in.	25.3	1.52	7.73	1.89	58.01	1.08
1/4 in.	8 mesh	46.2	2.70	10.31	3.30	53.45	1.14
8 mesh	30 mesh	13.8	5.24	17.47	6.53	55.25	1.30
30 mesh		1.7	3.32	17.75	4.63	44.14	1.80

---

*As received.

BLANK PAGE

SECTION 5

DETAILS OF REFUSE PILE TREATMENTS

SILICATE MATERIAL

The sodium silicate solution used in the laboratory experiments to determine the lag time for gelation was produced by Philadelphia Quartz (type N)* and has the following composition:

% SiO_2 : 28.7
% Na_2O: 8.9
% H_2O: 62.4
SiO_2/Na_2O: 3.22
Density: 41°Be (at 68 °F) , 1.39 g/ml

NEUTRALIZED PILE (PILE B)

A pile of coal mine refuse was neutralized by treatment with 3 ℓ of a waterglass solution containing 4% SiO_2. Neutralization was defined as the condition when the effluent solution of the pile during the waterglass treatment had the same pH as the fresh silicate solution. Examination of the pile showed that the particles of coal refuse were coated with a thin layer of some gel-like material. This coating did not block the flow of water through the pile, but did tend to prevent contact of the water with the surface of the coal.

SILICA GEL: SURFACE TREATMENT (PILE C)

It was intended that one pile of coal mine refuse should have a thin layer of silica gel to form a sealant layer. To accomplish this, it was necessary to determine the conditions under which waterglass would gel. It was known that acidifying the sodium silicate solution would cause gelation, and it was felt that it might be possible to allow the acid in the refuse pile to act as the acidifying material.

First, some tests were made to determine the gelling properties of the type N silicate. Reagent grade sulfuric acid was used to lower the pH. Distilled water was used for diluting the commercial silicate and making up all solutions.

---

*the use of this particular commercial product does not constitute endorsement or recommendation by the Federal Water Quality Administration.

Gel times were determined by adding a dilute solution of H_2SO_4 to sodium silicate solutions (in which the concentration of SiO_2 ranged from 1 to 28.0%), mixing well, and allowing the mixture to stand in 100-ml beakers kept at 25 °C until gelling.

The data obtained from these experiments are as follows:

Concentration: 1% SiO_2

pH	9.5	8.0	7.0	4.0
Gel time, sec	5×10^5	2100	2580	4×10^5

Concentration: 2% SiO_2

pH	8.5	6.5	6.0	2.5
Gel time, sec	1800	370	415	5×10^5

Concentration: 3% SiO_2

pH	9.0	8.5	7.5	6.5
Gel time, sec	320	170	90	250

Concentration: 4% SiO_2

pH	9.0	7.5	6.5	1.0
Gel time, sec	90	20	100	8 days

Several high concentrations of SiO_2 solutions (10 to 28.0% SiO_2) were tested for gel time at various pHs. Gel was formed instantly.

The data obtained from these experiments agree with the data published by Philadelphia Quartz Company, as presented graphically in Fig. 1.

Several experiments on small pyritic piles were set up to determine which waterglass should be used in treating the larger piles. In the first experiment, 250 g of the fresh, high sulfur coal refuse described above were slowly washed with 1000 ml distilled water. The washing was collected and analyzed. The analysis showed:

pH: 3.3
Acidity: 540 ppm as $CaCO_3$
Ferrous iron: 429 ppm
Total iron: 1177 ppm
SO_4: 475 ppm

This refuse was neutralized, without gel formation, with 100 ml of waterglass solution continaing 3% SiO_2 at pH 11.3.

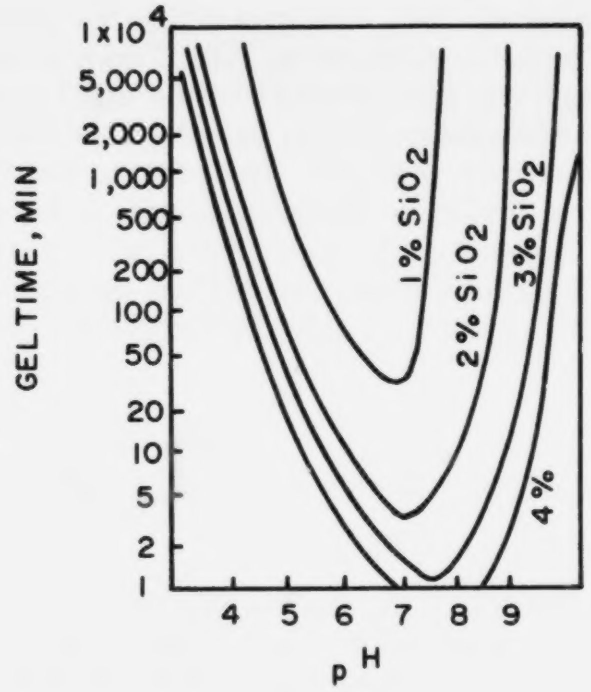

Fig. 1. Gel times at 25.0 °C of 3.22 ratio sodium silicate as a function of pH

The pile was slowly washed with 250 ml of distilled water and the effluent collected and analyzed. This analysis showed:

pH: 5.7
Acidity: 200 ppm as $CaCO_3$
Ferrous iron: 13.6 ppm
Total iron: 181.2 ppm
SO_4: 247 ppm

In the second experiment, gel was formed on the top of and partially inside a 500-g pile of fresh refuse by treating with waterglass solution containing 5% SiO_2 at pH 9.5. The treated pile was left for 1 hr to harden the gel and was then washed slowly with measured amounts of distilled water. The effluent pH was 4.0 after washing with 200 ml distilled water. Acidity was 100 ppm as $CaCO_3$.

To determine the reason that the AMD continued to be produced from this treated pile, it was cut into two halves. When examined, it was noted that gel was formed irregularly and that some pieces of refuse were not coated with gel. Water permeability of the pile was unimpaired.

Based on these experiments, it was decided to form the gel on Pile C using a silicate solution containing 4% SiO_2 and to acidify the solution to pH 9.5 before application. The actual treatment of Pile C was accomplished by passing the solution through the pile several times until gelation occurred. The gel formed was somewhat nonuniform, but the treatment was continued until the entire pile was covered with gel. In order to increase the residence time of the silicate solution in the pile, some of the gel was formed by thickening the silicate solution with Cab-O-Sil, a very fine silica powder. This increase in residence time greatly simplified the formation of a continuous gel across the pile. A total of approximately 4 ℓ of concentrated waterglass was used.

ALUMINA/SILICA GEL: SURFACE TREATMENT (PILE D)

The difficulty in forming the silica gel on the pile prompted a search for better gelation methods. In addition to the thickening procedure described it was found that a strong, continuous gel could be formed rapidly by mixing the sodium silicate with sodium aluminate. In fact, this method worked too well and the gel formed before the solution could be applied to the pile. This situation was remedied by first treating a pile with 1 ℓ of sodium silicate diluted to a solution containing 4% SiO_2 and then immediately treating the pile with 10 ℓ of 5% sodium aluminate. A strong gel was formed, primarily on the surface of the pile; very little of the material ran through the pile.

ALUMINA/SILICA GEL: IN-DEPTH TREATMENT (PILE E)

Gel was formed by slowly spraying the pile with sodium silicate solution (SiO_2/Na_2O: 3.22) containing 4% SiO_2 in order to let the solution go deeply through the pile. This was followed by spraying with sodium aluminate solution having a concentration of 5%. This procedure was repeated until the gel formed a layer inside the pile and covered the surface. The difference between this treatment and that of Pile D was that the silicate solution was allowed to penetrate into the pile before the aluminate was added. Thus, when the aluminate was sprayed on, it could not form a sealant layer of gel on the surface, but had to penetrate into the pile to form a gel. Successive treatment finally formed a blocking layer which caused a fairly uniform layer of gel to be built up.

The pile was immediately disturbed and it was found that the gel indeed had formed in the interior, but did not fill all the spaces between the rock particles. This caused the washing water to pass very slowly through the pile (as compared to the relatively rapid flow of water through the untreated pile).

SECTION 6

RESULTS AND DISCUSSION

PILE TREATMENTS

Five test piles were set up during the course of the experimentation and were evaluated as described above. The treatments used are summarized as follows (details of the treatment procedures are given in Section 4):

Pile	Treatment
A	Control — No treatment
B	Neutralized pile — a minimum amount of sodium silicate solution was permeated throughout the pile to neutralize acid via reaction (5), while not forming a continuous gel
C	Silica gelled pile — sufficient silicate was used to form a coherent gel on the surface of the pile
D	Alumina/silica gelled pile — this treatment was similar to (C), except that sodium aluminate was added to form a more insoluble gel
E	In-depth alumina/silica gelled pile — a mixed gel was formed beneath the surface of the pile to obtain protection from errosion and mechanical disruption of the gel

TEST RESULTS

The pH and the dissolved iron content of the samples are shown in Figs. 2 through 6, the complete analysis of all the piles is given in Appendix II, Tables XXVI through XXX. The wash volumes used were converted to inches of water so that the results could be examined in terms of rainfall. Pennsylvania, for example, receives an average of 40 in. of rain per year.

One comment on the iron analysis is pertinent. Most of the analyses are for samples passed through conventional laboratory filter paper. Late in the program, it was demonstrated that this procedure was inadequate for

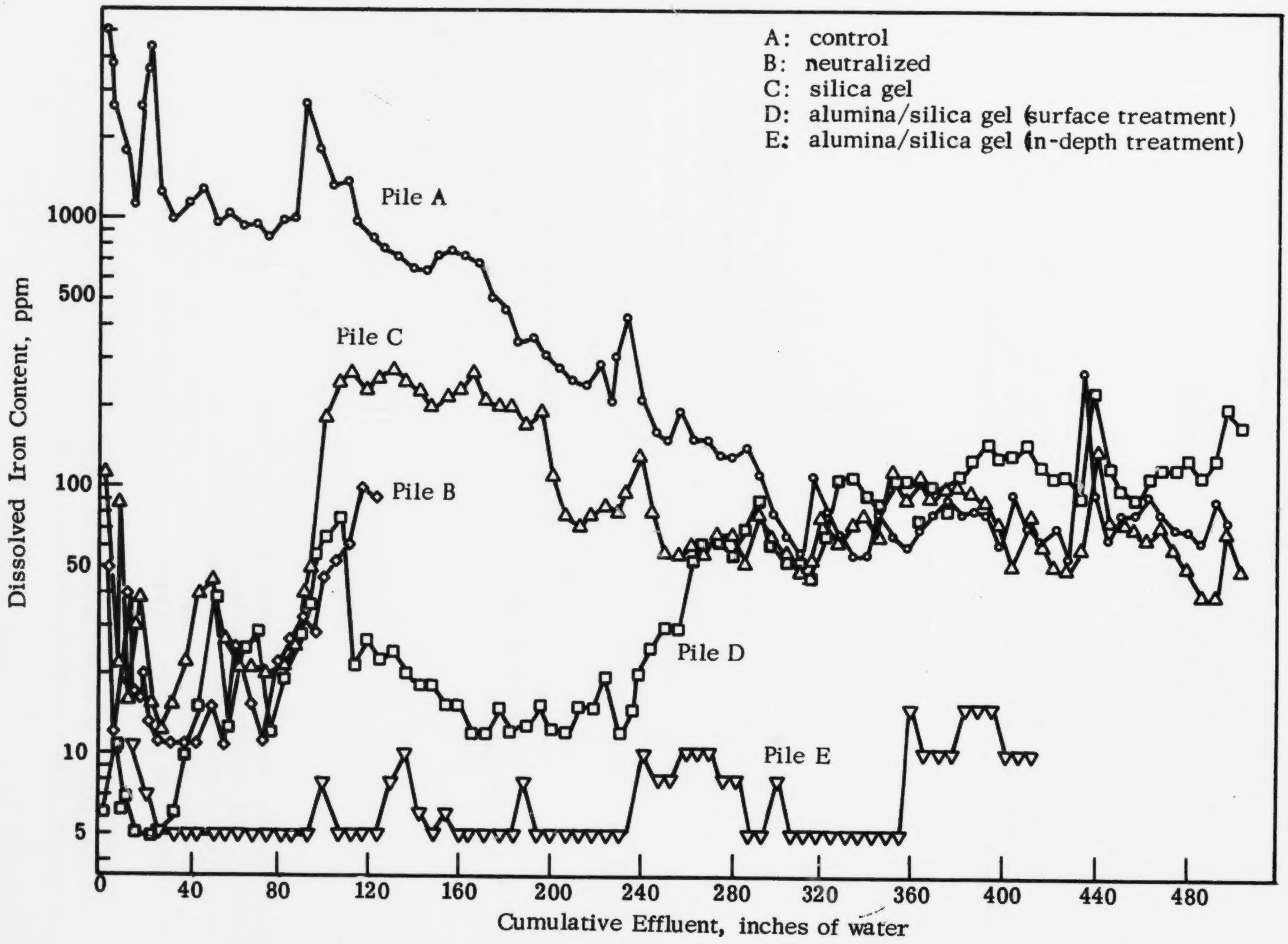

Fig. 2. Iron content of wash effluent from four test piles compared to control pile

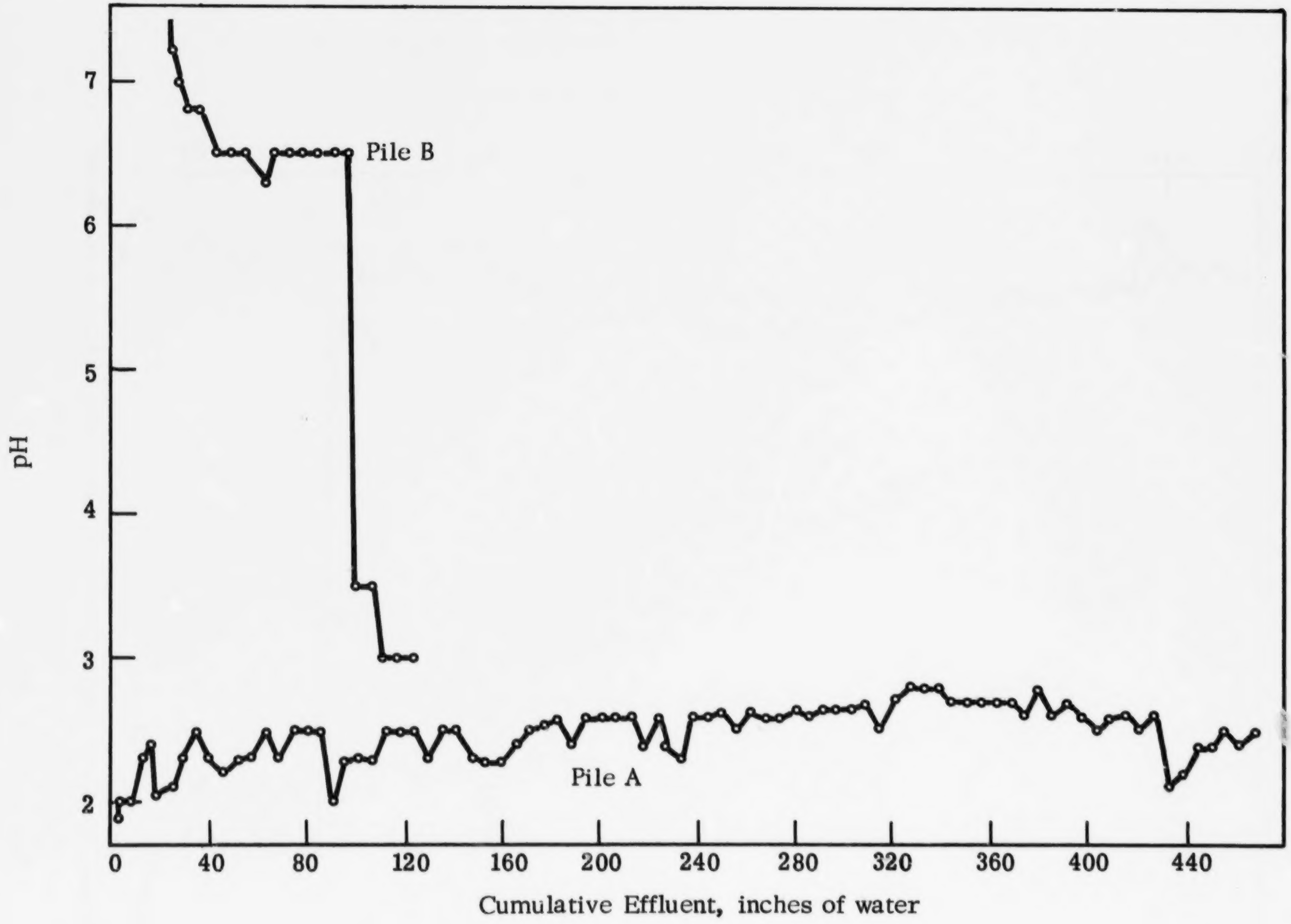

Fig. 3. pH of wash effluent from Pile B (neutralized pile) compared to Pile A (control)

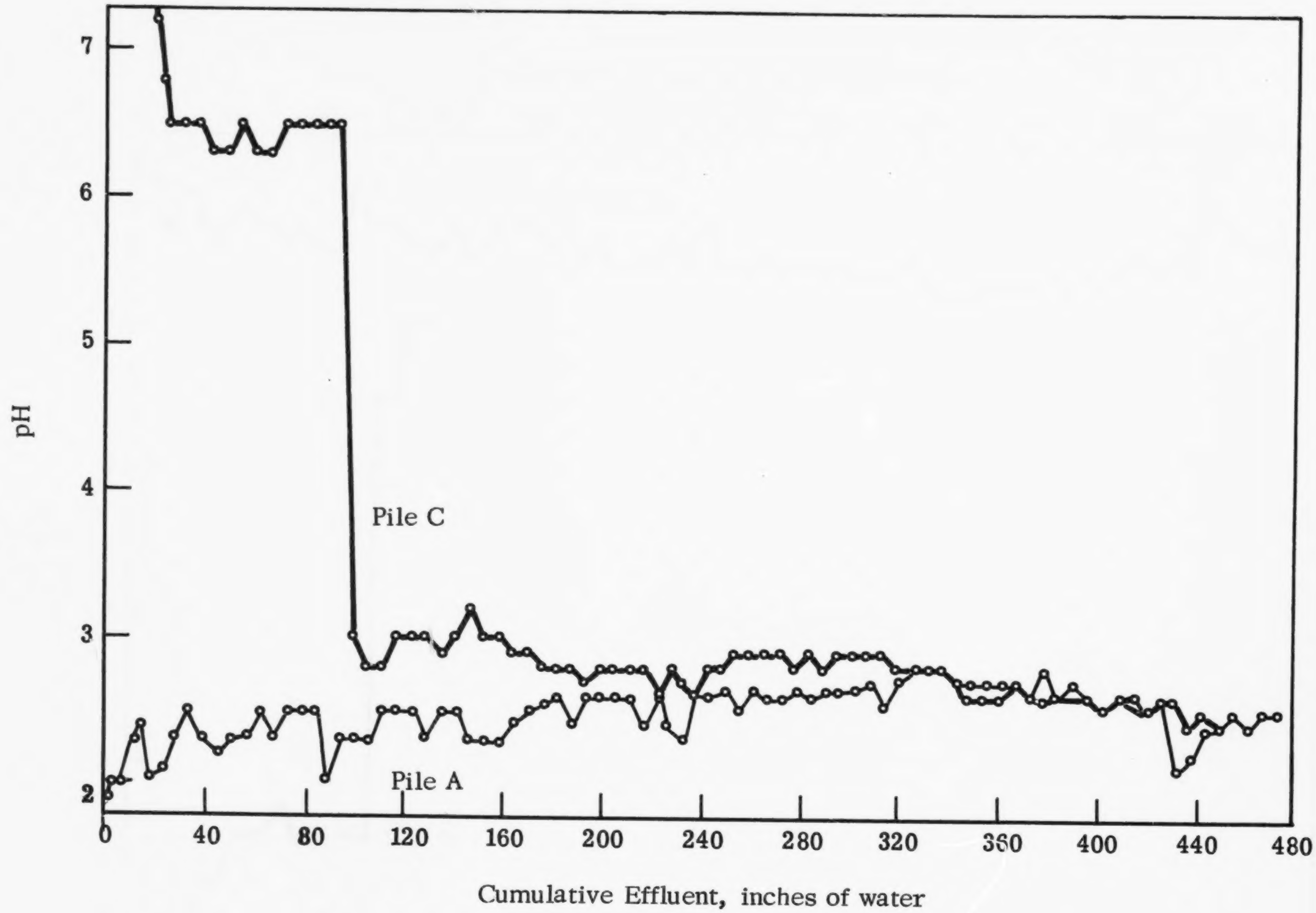

Fig. 4. pH of wash effluent from Pile C (silica gel-surface gel) compared to Pile A (control)

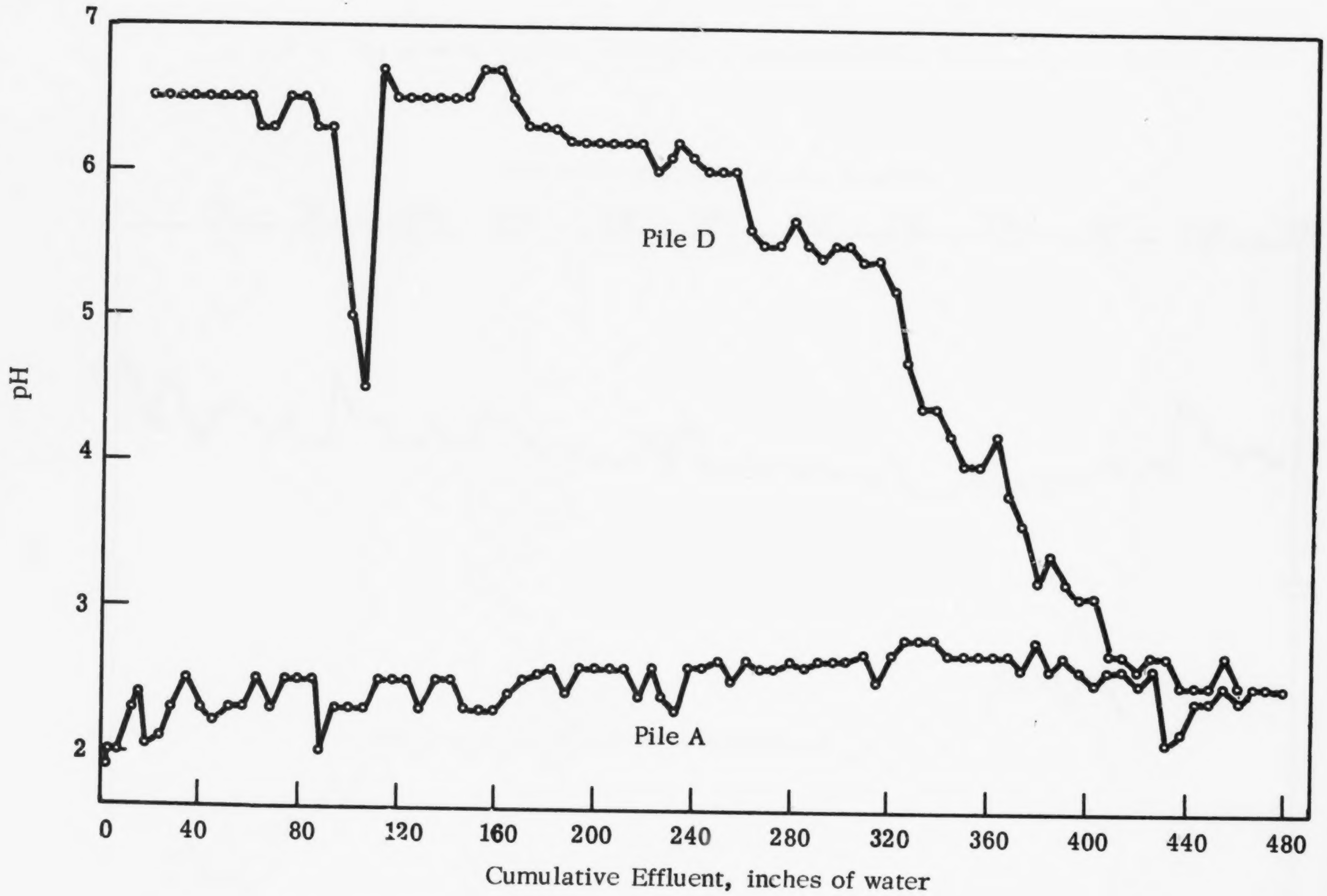

Fig. 5. pH of wash effluent from Pile D (alumina/silica gel - surface gel) compared to Pile A (control)

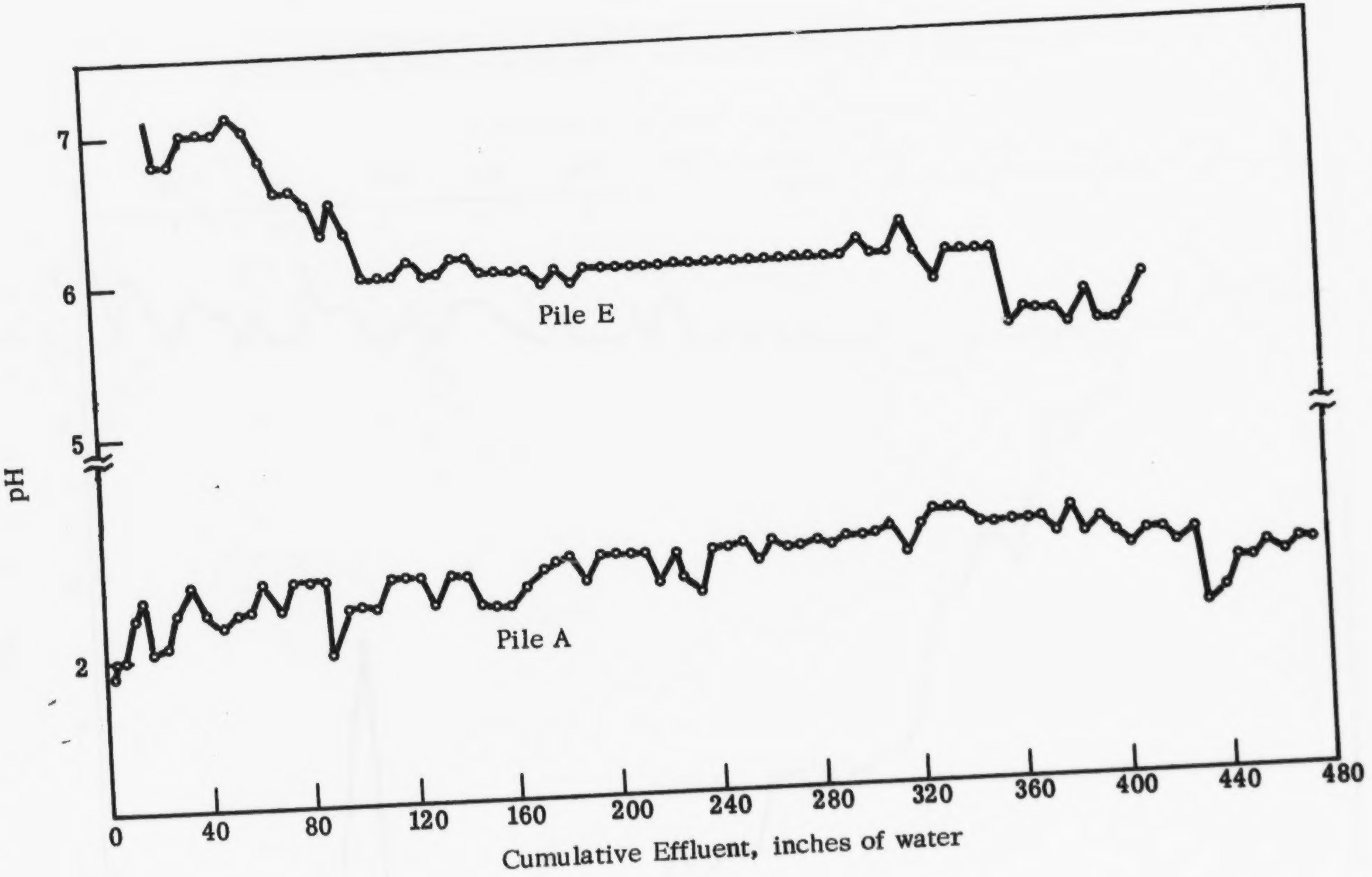

Fig. 6. pH of wash effluent from Pile E (alumina/silica gel-gelled in depth) compared to Pile A (control)

removing finely divided iron hydroxide. Calculations of the total soluble, chemically complexed ferric iron as a function of pH indicate negligible amounts (< 1 ppm) at and above pH 6. Experimental results confirm this conclusion. Therefore, the total dissolved iron values presented in Appendix II include suspended solid iron hydroxide for those samples with high pH. This applies to Piles B and C for the first 80 in. of equivalent rainfall; Pile D: 240 in.; Pile E: over 280 in.

DISCUSSION

Examination of the wash effluent analysis data for the control pile (A) shows that the effluent composition was comparable to that found in actual field studies.[8] The pH was about 2.0 and the iron content was 1000 to 5000 ppm (see Table XXVI in Apendix II).

The neutralization treatment (B) is effective for about 120 in. of equivalent rainfall in causing a reduction in the acid mine drainage produced by the washing of coal mine refuse. After this period, the treatment's effectiveness is reduced, but still yields acid flows at a lower level than untreated refuse.

This reduction in effectiveness is undoubtedly associated with the washing out of the silica from the pile (see Table XXVII in Appendix II) and as the silicate is washed out, the refuse is again exposed to the wash water. However, even after much of the silicate is washed out, the AMD production never approaches the level of the untreated pile (A). This is shown in Figs. 7 and 8 which compare the extent of iron and sulfur removal from the five different piles over several years of equivalent rainfall. (Note logarithmic scales on ordinates of both graphs.)

For treatment C (surface gelled with silica), as with the neutralized pile, the pH is increased and iron content is depressed. The silica is also slowly being washed out of this pile, although the rate is somewhat lower, i.e., about 40 ppm for Pile C versus 60 ppm for Pile B. It would be anticipated that the gel will eventually lose its integrity and allow the production of AMD. However, for the first 80 in. of equivalent rainfall, the appearance of the surface of the gel did not change appreciably and the wash water continued to run off the surface of the pile, not penetrating to the interior. The iron content of the effluent water was slowly increasing, but still remained an order of magnitude lower than the untreated pile.

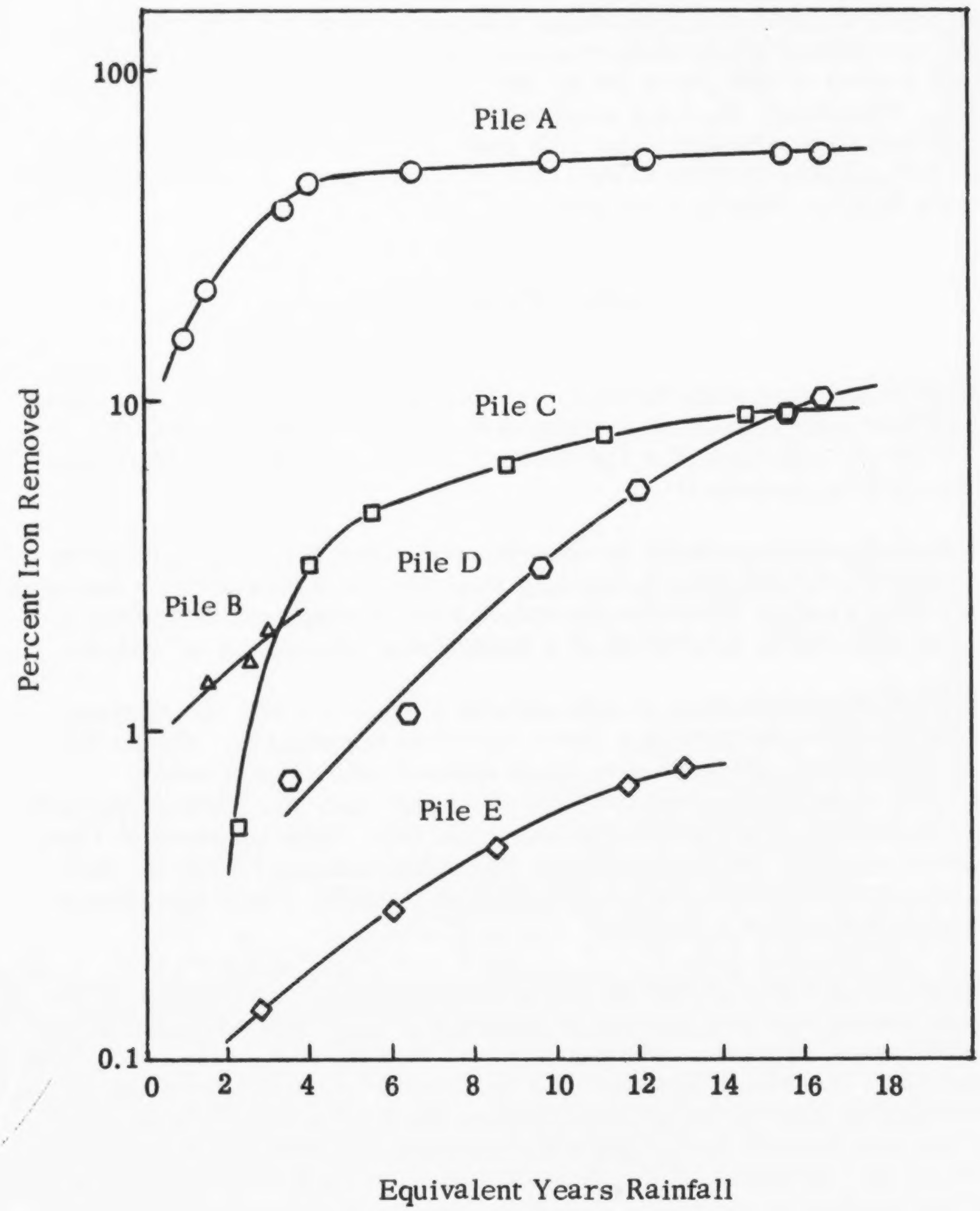

Fig. 7. Rate of iron removal from piles [A - control pile, B - neutralized pile, C - silica gel (surface treatment), D - alumina/silica gel (surface treatment), and E - alumina/silica gel (in-depth treatment)]

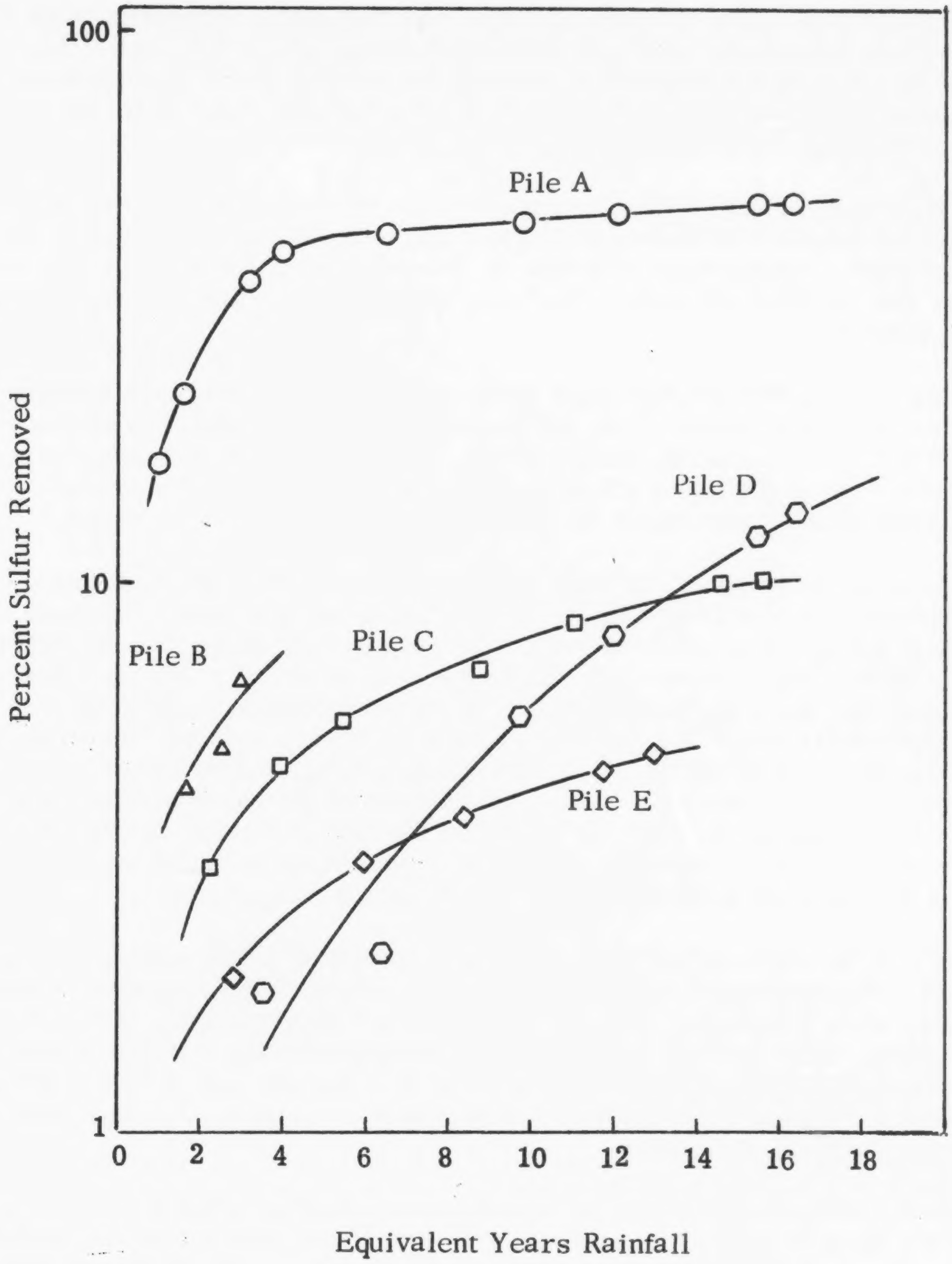

Fig. 8. Rate of sulfur removal from piles [A - control pile, B - neutralized pile, C - silica gel (surface treatment), D - alumina/silica gel (surface treatment), and E - aluminia/silica gel (in-depth treatment)]

After 80 in. of equivalent rainfall, the pile was disturbed. Several cracks were made in the suface of the gel and the washings were continued. The pile was then violently disturbed by turning the surface over. Examination of the interior of the pile showed very little internal gel, none of it continuous. Washings were continued.

The detailed data (Table XXVIII in Appendix II) show that breaking the gel on the surface of the pile allowed water to enter the interior, resulting in the formation of AMD. Comparison with Pile A, however, reveals that although the pH drops and the iron and sulfate increase sharply, all values are lower than the untreated pile.

Pile D was given a thin sealant layer of alumina/silica gel and was washed with water on a daily basis. It is evident that not only are the iron and sulfur compositions at reduced, stable levels, but the silica in the effluent is much lower than in the silica gel protected pile as expected. This result indicates that the pile will retain its stability for a longer period of time.

The continuous dropping of the wash water on certain spots on the surface of the pile caused local errosion faults in the continuous gel structure which were large enough to permit water to enter the interior of the pile and start to create AMD. These faults in the gel structure were due to the fact that the washing was not completely random, but tended to drop selectively in certain spots (this would not be the case under ordinary rainfall conditions). Since these faults were due to an experimental artifact and were not representative of the system in general, it was decided to seal the holes with gel and continue the test, making an effort to "rain" on the pile in a more random manner. The pile was therefore repaired, and it is obvious from the analysis data that the protection against AMD formation was resumed immediately.

The best results were obtained from the pile treated in depth with the alumina/silica gel. The decreased solubility of the gel enhanced the long term stability of the gel, while the deeper layer of gel increased its resistance to erosion and cracking. This fact can be confirmed upon considering that Pile E had been violently distrubed on day 1 of the treatment period, yet the wash effluent showed the lowest concentrations of pollutants. Clearly, this is a very promising treatment technique.

In summary, examination of the sulfur and iron removal rates for the various treatments show that they are all markedly superior to the untreated condition. Each treatment has its own advantages and disadvantages which will determine its use in specific situations. The neutralization technique appears to have the shortest lifetime, yet it is undoubtedly the cheapest since it would use the least amount of treatment material. Its lifetime can be increased through the use of aluminate in the neutralization procedure to reduce the solubility of the sealing precipitate.

The surface treatment with silicate gel alone is not as durable as that with the alumina/silica gel because of higher gel solubility, but it is cheaper than the mixture. The surface treatment with the alumina/silica gel is less expensive than the in-depth treatment, but the in-depth treatment is certainly the most effective. The proper treatment method must be chosen by optimization of both cost and effectiveness criteria.

BLANK PAGE

SECTION 7

GEL WEATHERABILITY TESTS

A series of tests were run to determine the effect of temperature extremes on the stability and effectiveness of the gel treatment. The tests were performed at two levels: small laboratory heating and freezing tests and larger outdoor freezing tests. The indoor tests were carried out by forming sealant layers of gel on 1-lb piles set up in small flat containers.

EFFECT OF HIGH TEMPERATURE ON ALUMINA/SILICA GEL

There were two purposes in performing high temperature tests on alumina/silica gel in refuse piles. One was to see how the gel withstood simulated summer conditions and the other was to see if the gel technique could be used on hot piles where the inside of the refuse pile was burning.

The "summer" test consisted of placing 1 kg of refuse in a shallow dish and forming the alumina/silica gel on the small pile. The treated pile was then placed under an infrared lamp which was adjusted so that the ambient temperature was between 85 and 90 °F. During the 1-week period of the test, the gel slowly dried out and took on the appearance of dried plaster.

At the end of the week, the pile was sprayed with water to determine the stability of the gel and its ability to prevent AMD generation. The washing was continued for 17 days (the results are shown in Table II). It was apparent that the gel was slowly washing away, and at the end of the test period there was little evidence of gel structure. However, when the pile dried out, the particles of refuse were covered with a very thin layer of white material which was apparently silica or alumina or a mixture of both. The results in Table II show that although the sealant layer of gel per se was gone, the residual silica or alumina continued to prevent AMD generation. It should be noted that in these tests 50 ℓ of water are equivalent to about 110 in. of rainfall.

Table II. Wash Analysis of Heated Pile
(Simulated "Summer" Test)

Day	Cumulative Volume of Wash,* ℓ	pH
1	0.5	12
4	2	8.3
7	5	7.5
9	10	7.2
11	15	7.2
14	20	7.0
15	30	7.0
16	40	6.8
17	50	6.5

---

* 0.46 ℓ of water is equivalent to 1 in. of rain.

A second test was run to simulate the treatment of a hot pile. Here, a 1-kg pile of refuse was treated with alumina/silica gel and placed in an oven at 130 °F, which is approximately the surface temperature of a hot pile. After 2 days of baking, a 15-day series of water washings was started. The effluent analysis is given in Table III. The visual results were very similar to the lower temperature test: the gel hardened during baking and was eroded during washing. Despite the fact that the continuity of the sealant layer was interrupted, no AMD was produced during the equivalent of 120 in. of rainfall.

The temporarily high pH of the effluent is undoubtedly due to the washout of the gel-forming materials as silicate and aluminate. Here again, the refuse retained a white layer when it was dried at the end of the equivalent of 110 in. of rainfall. This indicates that there is still residual silica adhering to the refuse which should seal the rock and thus prevent or at leat minimize AMD generation.

Table III. Wash Analysis of Heated Pile
(Simulated Hot Pile)

Day	Cumulative Volume of Wash,* ℓ	pH
1	5	10.8
2	10	8.0
3	15	7.2
4	20	7.0
7	25	7.0
8	30	7.0
9	35	6.8
10	40	6.8
11	45	6.6
14	50	6.6
15	55	6.5

---

* 0.46 ℓ of water is equivalent to 1 in. of rain.

"ANTIFREEZE" SELECTION

Several experiments were carried out to develop an antifreeze system that would prevent the the interstitial water in the gel from freezing. The tests consisted of gelling small laboratory piles weighing 500 g each, set up on a watch glass, and keeping them in the freezer at a temperature of -8 °C for various periods of time.

Sodium Chloride: Experimentation using NaCl as an antifreeze, in which the concentrations of the solution range from 5 to 10%, showed that the higher concentrations of NaCl form a water soluble gel with the silicate solution alone. When 500-g laboratory piles were gelled by adding 10% NaCl to the alumina/silica gel (in which the concentration of SiO_2 ranged from 5 to 10%), a gel was formed that resisted freezing at −8 °C. However, when the pile was sprayed with water, the NaCl was washed out. The chemical analysis showed that 93% of the added NaCl was removed during washing.

Calcium Chloride: This salt was ineffective as an antifreeze additive, since it formed a gel with the silicate solution which broke on freezing. At the same time, it reacted with sodium aluminate and formed a white precipitate of $Ca(OH)_2$.

Ammonium Chloride: These experiments showed that a water soluble gel was formed by the addition of NH_4Cl to the silicate solution with the release of NH_3 gas. Again, chloride ion was detected in the wash effluent. Also, NH_4Cl reacts with the sodium aluminate to yield the gelatinous precipitate of aluminum hydroxide.

Ethyl Alcohol: This material formed a strong gel with the concentrated solution of silicate, but the gel was found to be soluble in water. When we tried to mix ethyl alcohol with sodium aluminate (5%) and then added this mixture to a waterglass solution containing 4% SiO_2, it was found that the resultant gel has some solubility in water. The solubility of the gels formed using ethyl alcohol prevents its use as an antifreeze additive.

Prestone Ethylene Glycol: This material was also ineffective, since it formed a soluble gel.

Polyethylene Glycol 400: This material was also ineffective, since it formed a soluble gel.

Propylene Carbonate: This material formed a gel which was found to decompose when sprayed by acid mine water. Carbon dioxide gas was evolved, indicating that the carbonate was decomposed by the acidic water, thus destroying the gel.

Polyethylene Glycol 20,000: This material formed freeze-resistant gels when added to the silicate and aluminate mixtures. The concentrations of polyethylene glycol 20,000 used ranged from 5 to 10%. This was added to silicate solutions containing from 4 to 8% SiO_2 and sodium aluminate solutions containing 5 to 10% aluminate.

At low additive concentrations, the gel was quite weak in consistency. Although the higher concentrations gave stronger gels, it was found that this gel tends to separate from rock particles on spraying with water.

Glycerin: When glycerin was added (10% concentration) to the silicate and sodium aluminate, it produced a gel with characteristics similar to those produced from polyethylene glycol 20,000.

EFFECTS OF LOW TEMPERATURE ON ALUMINA/SILICA GEL

Two outdoor tests were set up to evaluate the effect of low temperatures on the alumina/silica gel. Both were performed in 3-gal pails containing about 25 lb of the refuse. One sample was treated with the gel in a manner similar to Pile E of the large scale test group, while the other sample was treated with a gel containing 0.5% by weight of polyethylene glycol (20,000).

Both pails were placed outdoors in an exposed place and allowed to endure the full effect of a New England winter. During the 45 days of the test, the temperature ranged between 3 and 53 °F. There was snow on 8 days and rain on 7 days. At the end of this 6-week period, the pails were examined and it was found that virtually no gel was visible. Upon drying, a layer of white material, which was probably residual alumina and silica, could be seen on the surface of the refuse pieces.

The liquid that had collected in the bottom of each pail was drained out and analyzed with the results shown in Table IV. It is clear that although the gel was no longer sealing the refuse, the acid production of the material was very low. It should be noted that the pails did not have drain holes in the bottom so the water could not drain out, thus the refuse was soaked in water for much of the 6 weeks of the test.

Table IV. Analysis of Collected Water From Outdoor Test

Test	pH	Acidity, ppm $CaCO_3$	Soluble Silica, ppm
With antifreeze	5.9	30	50
Without antifreeze	5.8	50	80

In order to see if the refuse that had been used in this test was still protected from producing AMD under more normal drainage conditions, samples from each test were placed in a dish and washed with water. The washings were collected and analyzed as shown in Table V. It would seem that the residual alumina and silica on the refuse surface maintained a protective layer, despite the absence of a coherent gel, and still prevented the production of AMD.

Table V. Analysis of Effluent Water From Washing Refuse Used in Outdoor Test

Test	pH	Acidity, ppm $CaCO_3$	Soluble Silica, ppm
With antifreeze	6.2	10	15
Without antifreeze	6.1	15	20

SECTION 8

TREATMENT OF ACID MINE DRAINAGE

SILICATE TREATMENT OF ARTIFICIAL ACID WATERS

The purpose of these experiments was to study the reaction of ferrous and ferric ions (present as sulfates) with silicate ions (present as waterglass) over a range of concentrations. The goal was to determine the effectiveness of waterglass in precipitating or complexing the iron.

The test procedure was to add 10 ml of ferrous (or ferric) sulfate solution of a chosen concentration to 10 cc of sodium silicate (waterglass) solution of a given concentration. The iron was kept in the range of 100 to 1200 ppm in order to simulate actual acid waters. After the reagents were mixed, the solution was filtered to remove any resultant precipitate and the filtrate was analyzed for pH and iron concentration. The filtrate was then treated with 0.5 ml of concentrated (10%) sodium aluminate solution to test the presence of free iron ions in the presence of silicates. It had been determined previously that the aluminate would precipitate free iron, but would not react with iron in any complex form. The aluminate-treated solution was filtered to remove precipitates and the filtrate was again analyzed for pH and iron content.

Table VI presents the raw data obtained when ferric sulfate was treated with waterglass and sodium aluminate. Examination of the data shows that there are three different situations:

1. No precipitate from silicate addition and no precipitate from aluminate addition. In this case, it is clear that the addition of the silicate caused the complexing of the iron into soluble iron silicates. The addition of the sodium aluminate could not break the iron silicate complex, although the aluminate would ordinarily precipitate all the iron. The analytical procedure for determining iron was chosen so that both free iron ions and complexed iron could be detected.

2. No precipitate from silicate addition, but some precipitate from aluminate addition. It appears that in this case the addition of silicate caused some of the iron to complex, but not all of it. When the aluminate is added, the free iron ions are precipitated.

Table VI. Treatment of Ferric Sulfate With Waterglass and Sodium Aluminate

Fe^{3+} Concentration,* ppm	Treatment	Silicate Concentration,* M				
		0.4	0.2	0.02	0.01	0.004
2122 (pH = 1.9)	Silicate	No ppt pH = 10.8 [Fe] = 1050	No ppt pH = 6.8 [Fe] = 1050		No ppt pH = 2.2 [Fe] = 1040	No ppt pH = 2.2 [Fe] = 1040
	Aluminate	No ppt pH = 11.5 [Fe] = 1050	No ppt pH = 9.3 [Fe] = 1040		Yellow-brown ppt pH = 6.5 [Fe] = 0	Yellow-brown ppt pH = 6.5 [Fe] = 0
424 (pH = 2.4)	Silicate	No ppt pH = 11.3 [Fe] = 210	No ppt pH = 11.0 [Fe] = 210	Yellow-brown ppt pH = 2.9 [Fe] = 67	Yellow-brown ppt pH = 2.6 [Fe] = 178	Yellow-brown ppt pH = 2.6 [Fe] = 160
	Aluminate	Glassy gel pH = 12.2 [Fe] = 210	No ppt pH = 11.7 [Fe] = 210	Yellow-brown ppt pH = 10.8 [Fe] = 0	Yellow-brown ppt pH = 10.2 [Fe] = 67	Yellow-brown ppt pH = 10.1 [Fe] = 44

---

*After dilution, concentrations are one-half these figures.

Table VI. (Cont.)

Fe^{3+} Concentration, ppm	Treatment	Silicate Concentration, M 0.4	0.2	0.02	0.01	0.004
218 (pH = 2.4)	Silicate	No ppt pH = 11.4 [Fe] = 110	No ppt pH = 11.2 [Fe] = 110	No ppt pH = 7.8 [Fe] = 110	Yellow-brown ppt pH = 2.9 [Fe] = 15	Yellow-brown ppt pH = 2.8 [Fe] = 40
	Aluminate	No ppt pH = 11.6 [Fe] = 110	No ppt pH 11.7 [Fe] = 110	No ppt pH = 11.3 [Fe] = 110	No ppt pH = 11.3 [Fe] = 0	No ppt pH = 10.9 [Fe] = 40

3. Silicate addition causes precipitation, and aluminate addition produces further precipitation. In this case, the silicate causes the precipitation of the iron as iron silicate. The iron silicate precipitates at pH values below about 7, but not above that. Therefore, if insufficient silicate is added to raise the pH from the acid level of the iron sulfate solution to a point above 7, the iron silicate will precipitate. If the pH is raised above 7 by waterglass addition, the iron is complexed and cannot then be precipitated.

The amount of waterglass needed to cause the iron to complex without precipitating can be determined by means of a graph such as Fig. 9. Here, the iron and silicate concentrations in the mixed solution (from Table VI) are plotted for the condition where all the iron is complexed. The minimum silicate required for any concentration of iron is determined by drawing a line through the origin and the data points representing the least amount of silicate that was used to complex a given amount of iron. The ratio of silicate to iron along this line is a constant and has a value of six parts of waterglass (100% sodium silicate with a weight ratio of SiO_2/Na_2O of 3.22) to one part of iron. This is a rather high value and will undoubtedly prove to be very costly, but the work does establish the concept of being able to make the iron inert and not subject to precipitation. The advantage of this treatment would be that the acid mine water could be treated without the necessity of settling and collecting a hard to handle, low-solids precipitate.

A similar series of experiments was performed with ferrous sulfate solutions as shown in Table VII. The data are plotted in Fig. 10. It is not as obvious how the minimum line should be drawn, but using the origin and point A, a line can be drawn that will create a region that includes all other points. The minimum weight ratio is again about six parts silicate to one part iron; there is some evidence that suggests that the minimum line should be steeper than that drawn. This would give a lower ratio of silicate to iron, which can be derived from the fact that the pH of the solution at point A is still quite basic (pH = 10.3) and the minimum point should be close to pH 7 (that is, lower silicate content). In any case, the line is steeper than that drawn through point A, but not as steep as that drawn through point B which is outside the complexing region obtained from Table VII. The weight ratio for the line drawn through point B is 4.3 parts silicate to 1 part iron.

OXIDATION OF FERROUS TO FERRIC IN THE PRESENCE OF SILICATE

The previous experimentation raised the question of how stable the ferrous silicate complex was to oxidation of the iron. Since it is known that most of the iron content of acid waters is in the ferrous form, this might have some bearing on the treatment. An iron silicate complex solution was formed by

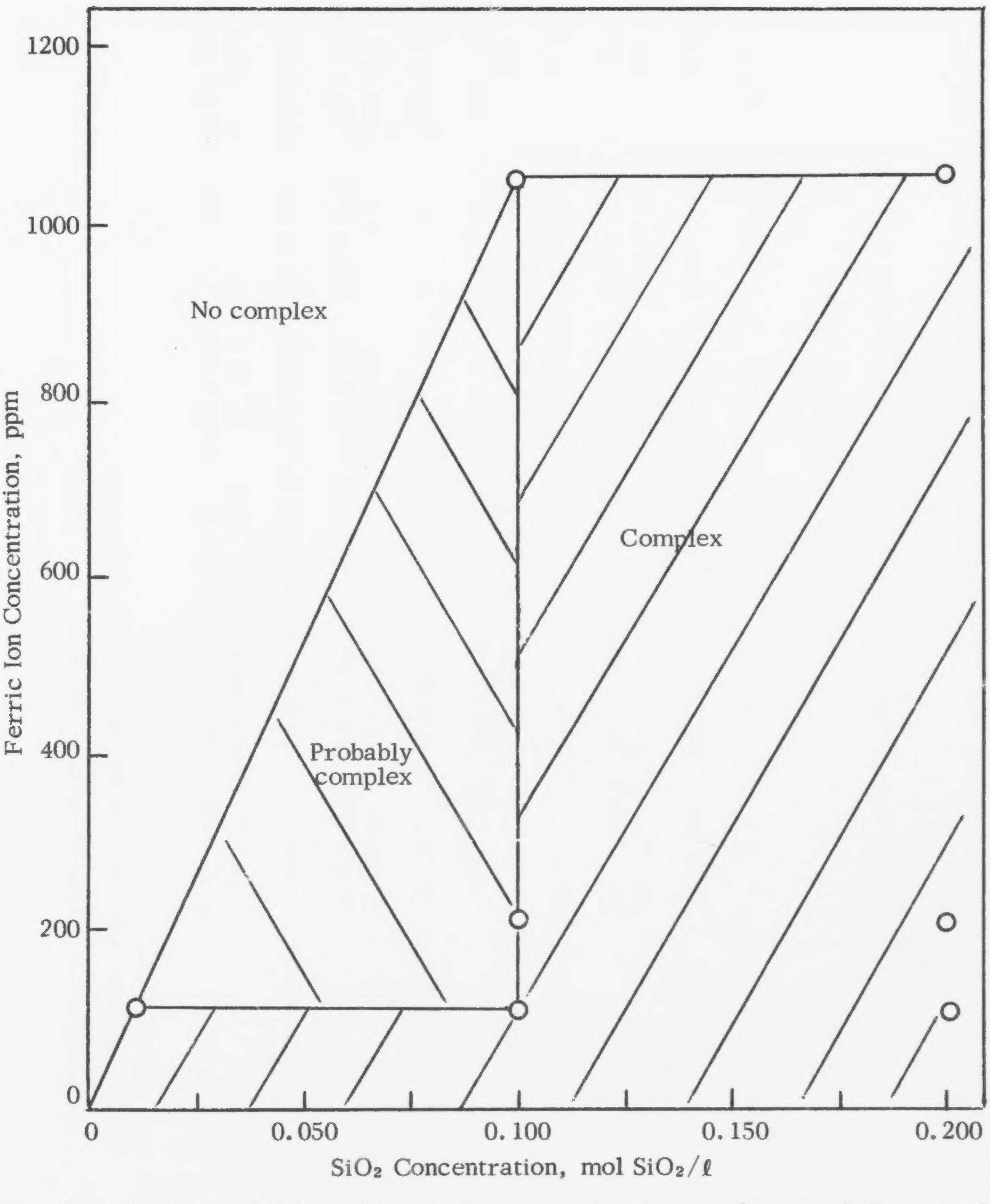

Fig. 9. Determination of the minimum amount of waterglass needed to complex ferric iron in ferric sulfate solution

Table VII. Treatment of Ferrous Sulfate With Waterglass and Sodium Aluminate

		Silicate Concentration,* M					
Fe^{2+} Concentration,* ppm	Treatment	0.4	0.2	0.04	0.02	0.01	0.004
2200	Silicate	Faint ppt† pH = 11 [Fe] = 1005	No ppt† pH = 10.3 [Fe] = 1095	Blue-green ppt pH = 5 [Fe] = 703	Blue-green ppt pH = 5.4 [Fe] = 893	Blue-green ppt pH = 4.7 [Fe] = 893	Blue-green ppt pH = 4.9 [Fe] = 972
	Aluminate	No ppt† pH = 12.3 [Fe] = 1005	No ppt† pH = 12.2 [Fe] = 1050	Blue-green ppt pH = 9.2 [Fe] = 0	Blue-green ppt pH = 9.2 [Fe] = 20	Blue-green ppt pH = 9.0 [Fe] = 0	Blue-green ppt pH = 6.5 [Fe] = 55
1050	Silicate	No ppt† pH 11.5 [Fe] = 530	No ppt† pH = 10.8 [Fe] = 530	Blue-green ppt pH = 6.5 [Fe] = 223	Blue-green ppt pH = 5.8 [Fe] = 357	Green ppt pH = 4.6 [Fe] = 424	Yellow ppt pH = 5.6 [Fe] = 480
	Aluminate	No ppt† pH = 12 [Fe] = 530	No ppt† pH = 12.3 [Fe] = 530	Blue-green ppt pH = 10.4 [Fe] = 0	Blue-green ppt pH = 10.2 [Fe] = 20	Green ppt pH = 10.0 [Fe] = 44	Green ppt pH = 10.1 [Fe] = 50

---

*After dilution, concentration are one-half these figures.

†The filtrate (or solutions) turned deep blue.

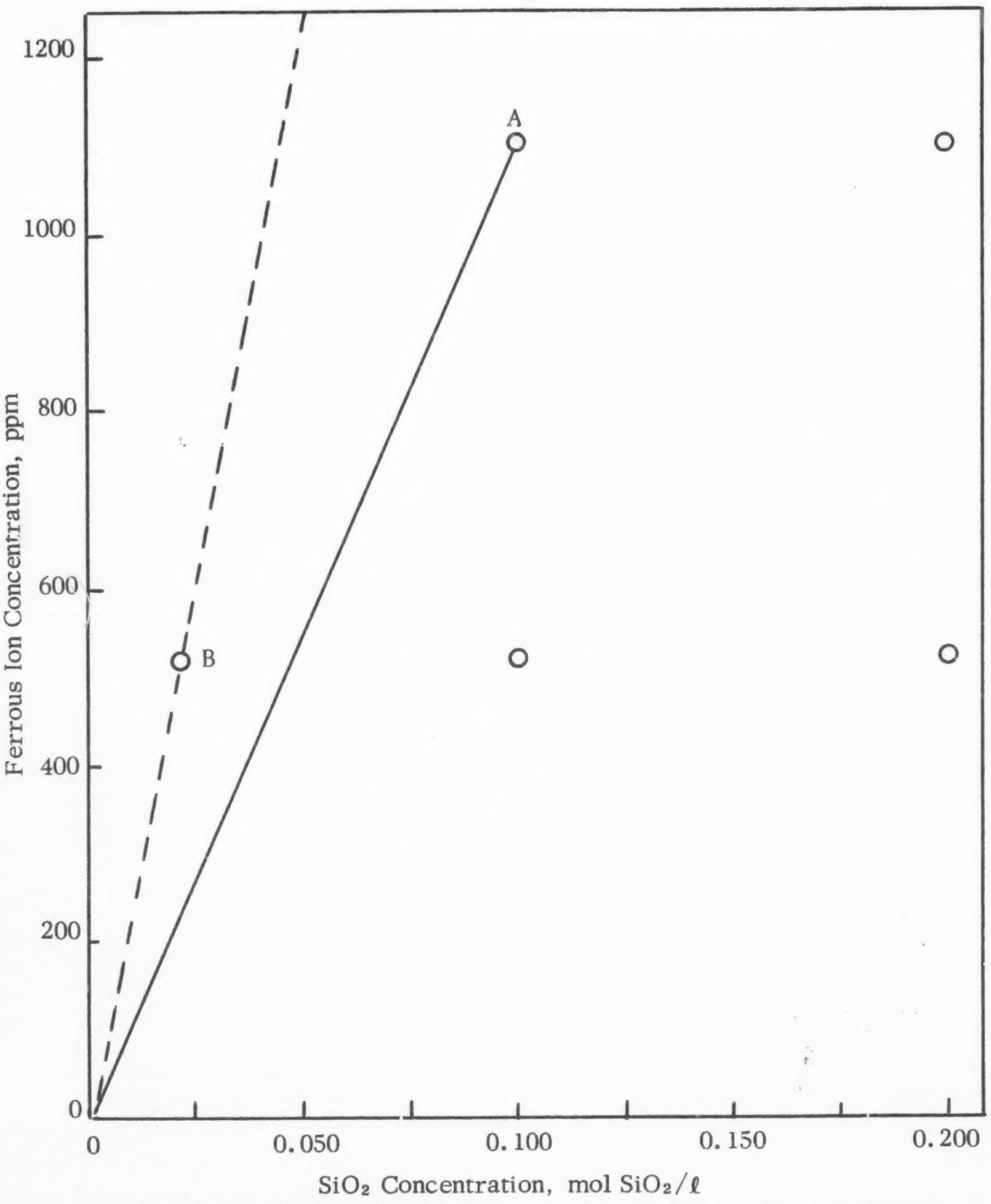

Fig. 10. Determination of the minimum amount of waterglass needed to complex ferrous iron in ferrous sulfate solution

mixing 100 ml of ferrous sulfate solution (2122 ppm as ferrous) with 100 ml of sodium silicate solution (0.15M). Examination of Fig. 10 shows that this mixture is in the band that should be fully complexed (and was verified by the fact that the resultant solution, which is 0.75M in silicate, has a pH of 9.3).

Portions of this mixture were analyzed for ferrous at various time intervals. For each sample of the mixture that was analyzed, a portion of the original ferrous solution was also analyzed for ferrous as a control. The results are shown in Table VIII and plotted in Fig. 11. The data show clearly that the presence of silicate accelerates the rate of ferrous oxidation. The fact that the control sample of ferrous sulfate did not appear to oxidize at all over a period of almost 3 days is somewhat surprising, although it is known that without aeration this oxidation takes place quite slowly.

Table VIII. Oxidation of Ferrous to Ferric in the Presence of Silicate

Time Elapsed, hr	Ferrous Concentration With Silicate, ppm	Ferrous Concentration Without Silicate, ppm	Amount Ferrous Oxidized, %
0.33	770	1060	27.4
1	614	1060	42.1
3	470	1060	55.7
5	357	1060	66.3
70	90	1060	91.5

PRECIPITATION OF FERROUS AND FERRIC IRON USING SODIUM ALUMINATE

Since experimentation showed that sodium aluminate could be used to precipitate all the iron in acid water, a series of experiments was run to determine the minimum amount of aluminate needed to do this and to compare the results with lime treatment.

The procedure used was to add the same volume of 10% sodium aluminate solution to different volumes of an iron sulfate solution of known concentra-

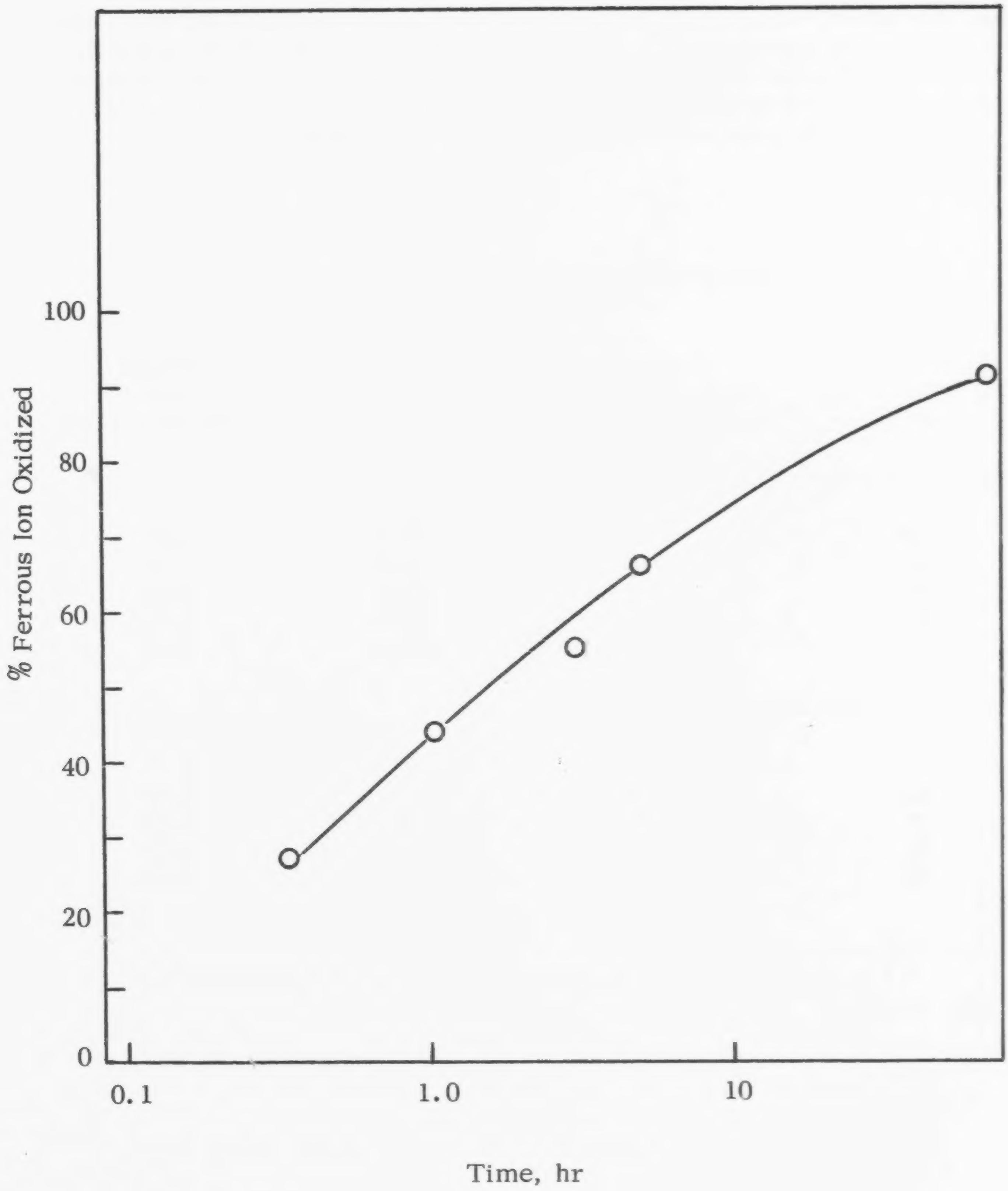

Fig. 11. Oxidation of ferrous to ferric in the presence of silicate

tion. The precipitate was filtered out and the filtrate analyzed for iron. The results of these experiments for ferrous and ferric solutions are shown in Table IX. If these data are plotted, as in Figs. 12 and 13, it can be determined that 2.48 g of sodium aluminate are needed to precipitate 1 g of ferrous iron and 1.24 g are needed to precipitate ferric iron.

Table IX. Precipitation of Ferrous Iron by Sodium Aluminate

Volume of Iron in Solution, ml	Iron Concentration in Filtrate, ppm	Amount Iron Precipitated, %	Weight Ratio, Aluminate: Iron
Ferrous Solution (1040 ppm) *			
60	352	66.2	1.60
50	218	79.0	1.92
45	128	87.7	2.14
40	34	96.7	2.40
35	0	100.0	2.75
Ferric Solution (1060 ppm) *			
60	358	66.4	0.79
50	235	77.9	0.94
45	156	85.2	1.05
40	45	95.8	1.18
35	0	100.0	1.35

---

*0.5 ml of 10% sodium aluminate added to given volumes of iron sulfate solution.

PRECIPITATION OF FERROUS AND FERRIC IRON USING LIME

Experiments were run to precipitate ferrous and ferric iron with lime to compare the results with those for sodium aluminate precipitation. Varying weights of lime (CaO) were added to identical volumes of ferrous sulfate and ferric sulfate solutions containing known iron concentrations. The mix-

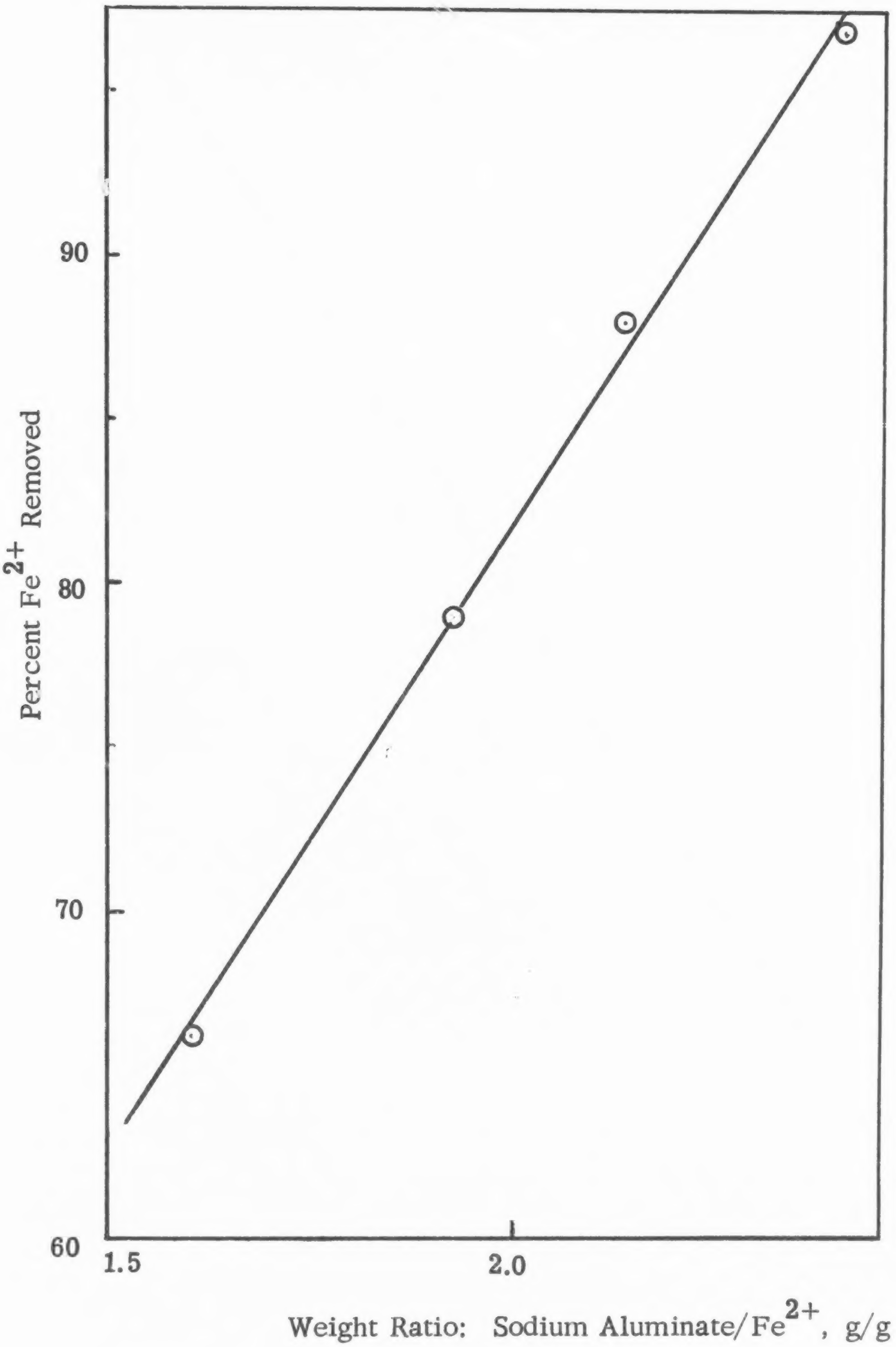

Fig. 12. Amount of sodium aluminate needed to precipitate ferrous iron

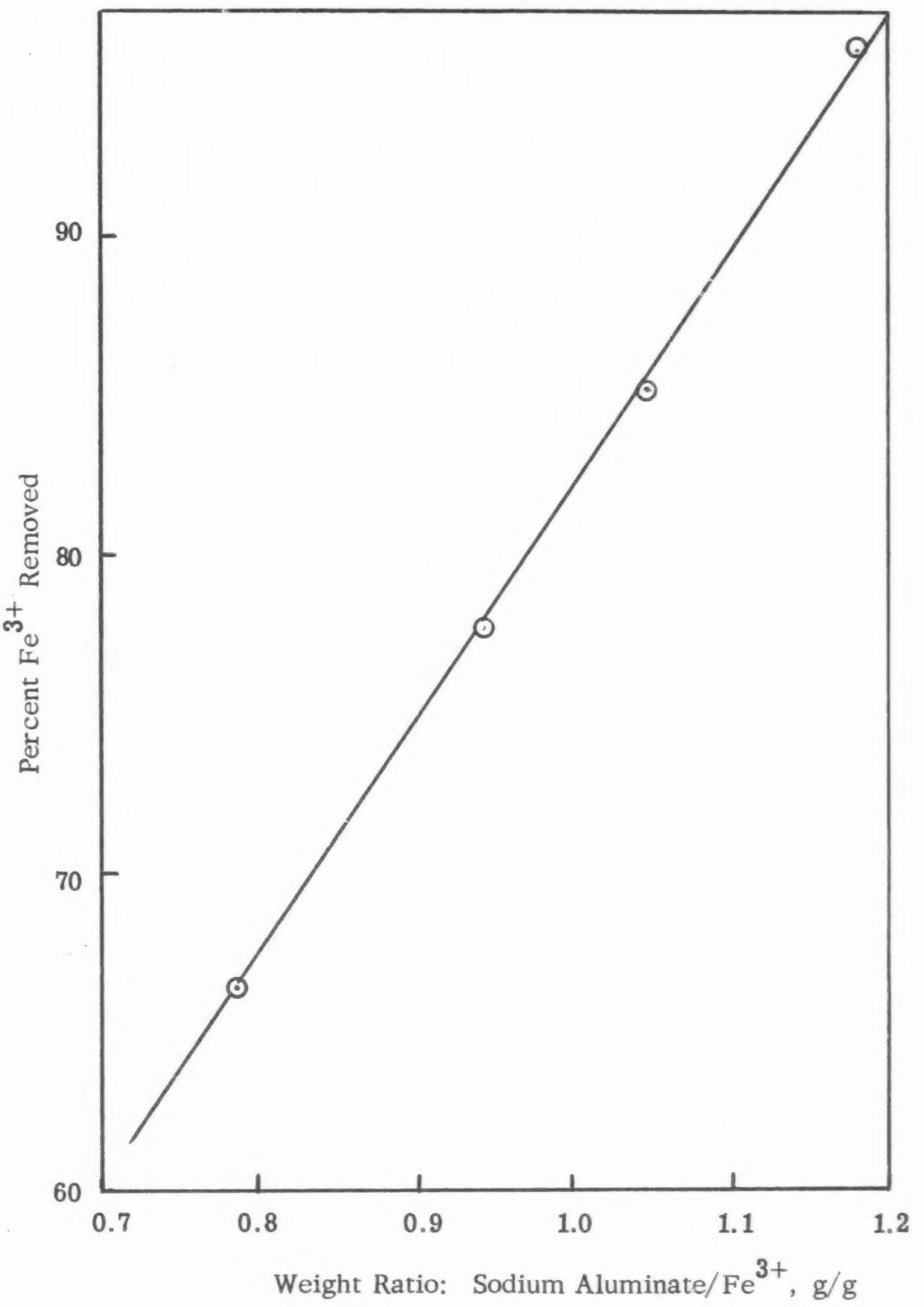

Fig. 13. Amount of sodium aluminate needed to precipitate ferric iron

tures were shaken vigorously for at least 3 hr, then filtered and the filtrate analyzed for iron. The composition of the mixtures and the analytical results are shown in Table X. The results are shown graphically in Figs. 14 and 15, and indicate that the precipitation of ferrous and ferric iron requires about 1.2 and 1.3 g of lime per gram of iron, respectively. For the ferric iron, this is about the same as with sodium aluminate and is about half the amount needed for ferrous precipitation with aluminate.

Table X. Precipitation of Ferrous and Ferric Iron With Lime

Weight of CaO Added to 50 Ml of Iron Solution, g	Iron Concentration in Filtrate, ppm	Amount Iron Precipitated, %	CaO/Fe*
Ferrous Solution (1016 ppm)			
0.03	390.9	61.5	0.590
0.04	234.5	76.9	0.787
0.05	145.2	85.7	0.984
0.06	—	100.0	1.181
Ferric Solution (1005 ppm)			
0.02	815.4	18.9	0.397
0.03	636.7	36.6	0.595
0.04	446.8	55.5	0.793
0.05	278.2	72.2	0.993

$$*\text{CaO/Fe} = \frac{\text{Weight of CaO}}{50 \times \text{ppm Fe} \times 10^{-6}}$$

SETTLING RATE AND SOLIDS CONTENT OF IRON PRECIPITATES USING LIME AND SODIUM ALUMINATE

Settling Rates: Solutions containing about 1000 ppm Fe were treated as shown in Table XI . The mixtures were shaken vigorously for 30 min and

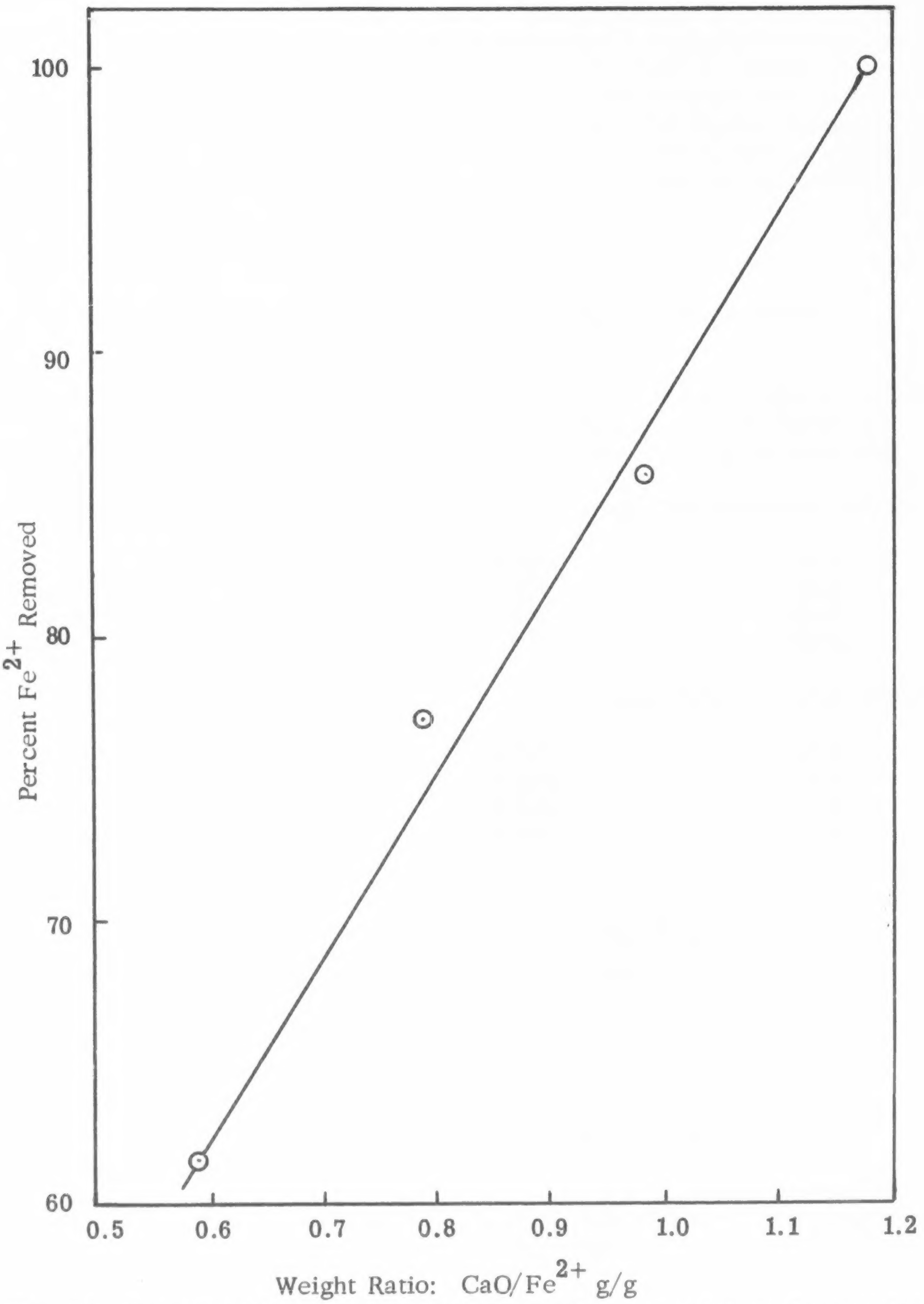

Fig. 14. Determination of amount of lime needed to precipitate ferrous iron

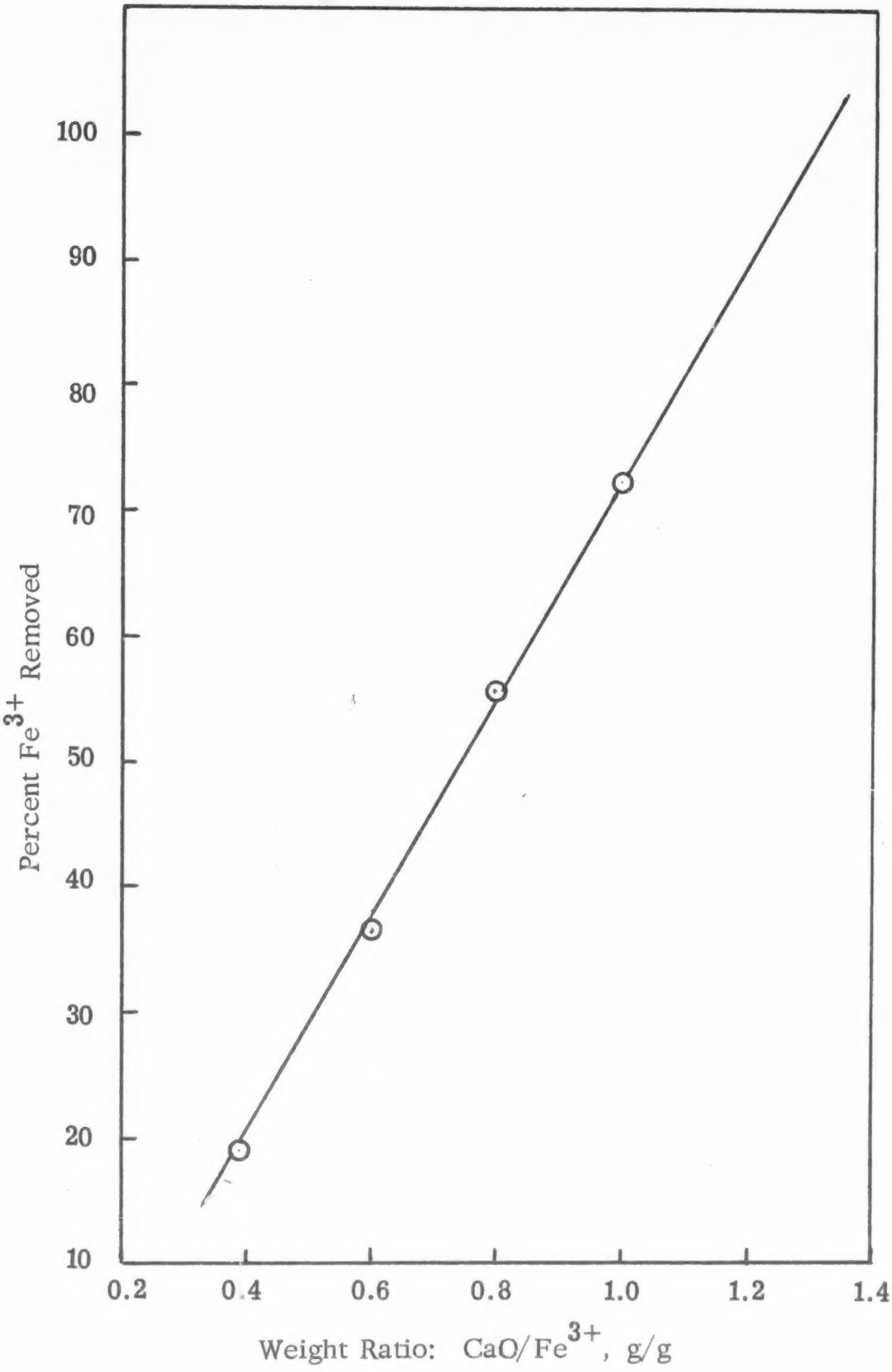

Fig. 15. Determination of amount of lime needed to precipitate ferric iron

one of each type (sample numbers 1, 3, 5, 7) were put in graduates and allowed to settle. The level of the top of the suspension was recorded as time passed using the graduations on the cylinder for reference (500 at the top of the graduate). The readings taken are shown in Table XII and plotted graphically in Figs. 16 and 17. It is quite obvious that there is no advantage in settling rate to using sodium aluminate to precipitate iron from acid mine drainage, in fact the rate is slower and more sludge is produced.

Table XI. Iron Solution Treatments

Test No.	Iron Solution	Aluminate Added	Lime Added
1	500 ml (1000 ppm Fe^{2+})	1.5 g in 20 ml H_2O	
2		1.5 g in 20 ml H_2O	
3			1.2 g in 20 ml H_2O
4			1.2 g in 20 ml H_2O
5	500 ml (1000 ppm Fe^{3+})	1.4 g in 20 ml H_2O	
6		1.4 g in 20 ml H_2O	
7			1.5 g in 20 ml H_2O
8			1.5 g in 20 ml H_2O

Solids Content of Iron Precipitates: The remaining samples from Table XI (numbers 2, 4, 6, 8) were placed in separatory funnels and allowed to settle for 75 min (except sample no. 2 which settled for 4 hr). The settling time chosen was that time at which the suspension did not seem to be settling further. The settled sludge was then removed from the bottom of the funnel and its solids content determined. The results of these experiments are shown in Table XIII,

The results of all the tests shown here indicate that there is no advantage to using sodium aluminate to precipitate iron from acid mine drainage.

Table XII. Settling Rates

Time, min	Test Sample Fe^{3+}/ Aluminate (5)*	Fe^{3+}/ Lime (7)	Fe^{2+}/ Aluminate (1)	Fe^{2+}/ Lime (3)
0	500			
1			492	
5	490	390		
8	455			
10	430	290		470
12	405			
14	385			
15		190		
17	357			
20	335	150		360
23	308			
25		125		
30	260	112		282
35		105		
36	232			
40				240
45	210			
50		93		215
55	190			
60			480	200
65	180			
70				
75	170			190
90			465	
120			455	
150			440	
180			430	
210			417	
240			405	
3 days		50		

---

*Numbers in parentheses refer to test numbers in Table VII.

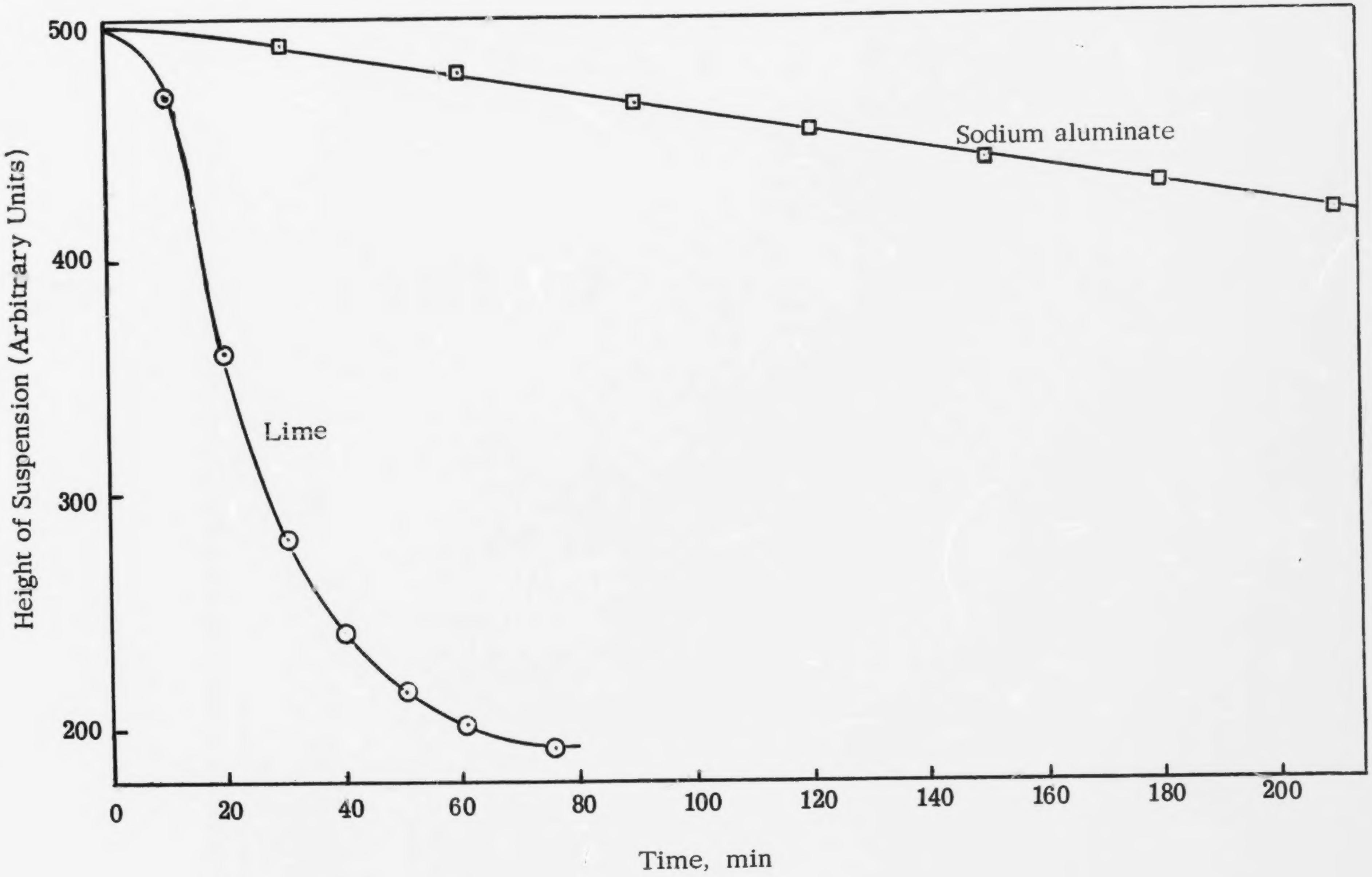

Fig. 16. Comparison of settling rates using sodium aluminate and lime to precipitate ferrous iron

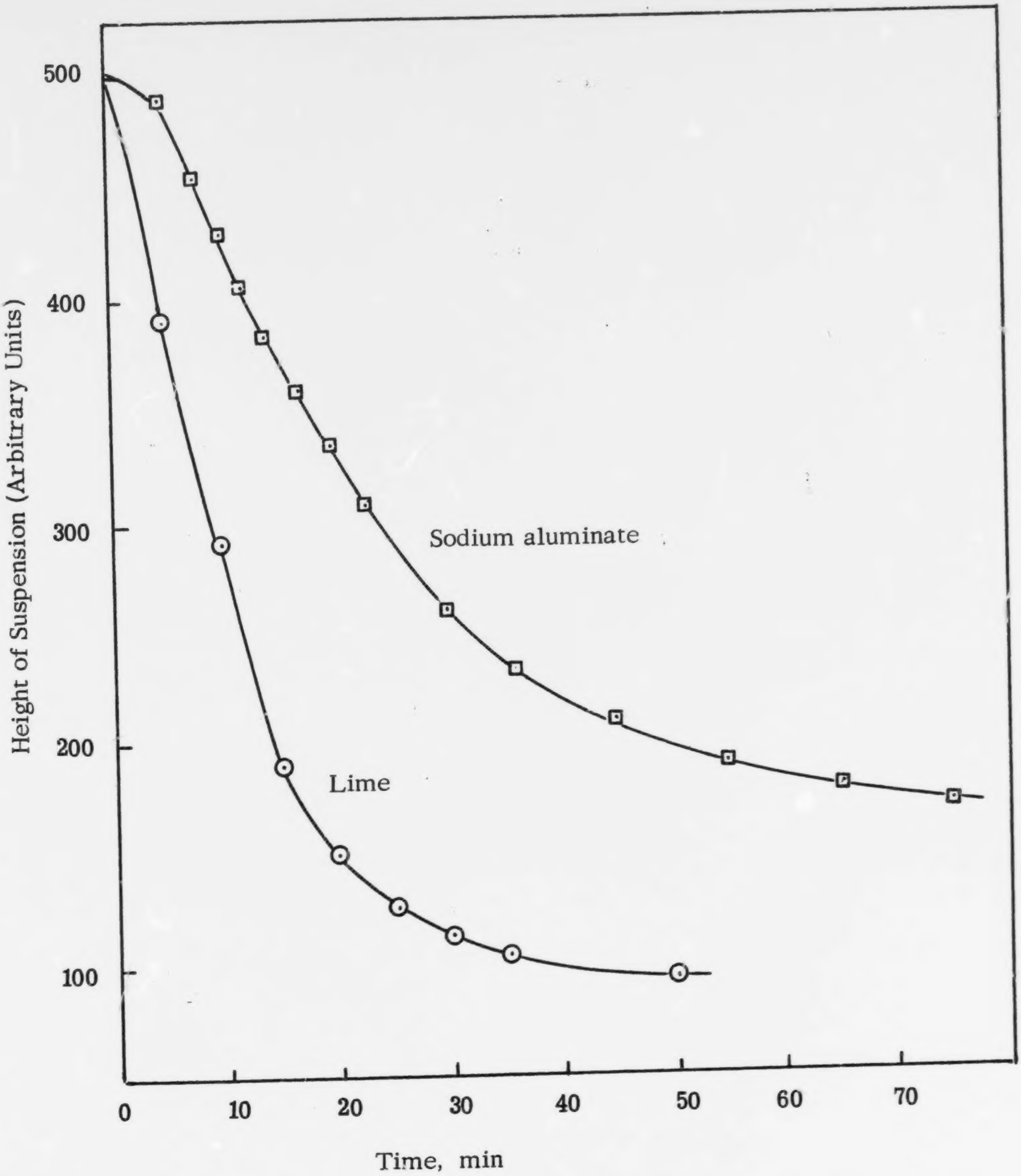

Fig. 17. Comparison of settling rates using sodium aluminate and lime to precipitate ferric iron

Table XIII. Solids Content of Iron Precipitates

	Weight of Sludge, g	Weight of Dry Ppt, g	Solids Content, %
Fe^{2+}/aluminate (2)	45.34	0.19	0.4
Fe^{2+}/lime (4)	25.52	0.36	1.4
Fe^{3+}/aluminate (6)	23.75	0.55	2.3
Fe^{3+}/lime (8)	16.67	0.55	3.3

SECTION 9

OTHER EXPERIMENTS

OPTIMIZATION OF ALUMINIA/SILICA GEL CONCENTRATION

In order to optimize the composition of the alumina/silica gel for in-depth gelation, a series of tests was run using several different combinations of solution concentrations. The criteria used for optimization were gelation time and the strength of the gel. The results are given in Table XIV. The data in this table give a qualitative evaluation of the consistency of the gel as well as the time it took to gel.

The procedure used was to mix 10 ml of a silica solution of the concentration shown in the table with 10 ml of an aluminate solution (concentration shown in the table). Thus, the final solution had a concentration of each component equal to one-half the concentration given in the table. The optimum solution was considered to be a mixture of 3% silica solution with 3% aluminate, or a final solution containing 1.5% of each.

Table XIV. Optimization Studies for Alumina/Silica Gel Composition Showing Gel Time (sec) and Gel Consistency

Wt % SiO_2 in Water-glass Solution	Wt % Sodium Aluminate in Solution				
	1	2	3	4	5
1	No gel (60)	No gel (60)	Very weak gel (1260)	Weak gel (900)	Weak gel (480)
2	No gel (60)	Weak gel (1800)	Fair gel (410)	Good gel (250)	Good gel (135)
3	No gel (60)	Very weak gel (2100)	Good gel (315)	Excellent gel (160)	Excellent gel (73)
4	No gel (60)	Very weak gel (2400)	Good gel (270)	Excellent gel (106)	Excellent gel (55)
5	No gel (60)	Very weak gel (2400)	Good gel (230)	Excellent gel (100)	Excellent gel (52)

STABILITY OF ALUMINA/SILICA GEL IN CONTACT WITH AMD

In order to determine the stability of the alumina/silica gel when it was contacted with AMD, a series of static and dynamic tests was run. The static tests consisted of forming the gel either in the bottom of a beaker or jar and then pouring in an AMD formed by passing water over the coal mine refuse. The system was allowed to sit for several weeks. In the static test, the gel was formed in a beaker and then transferred in pieces into a jar. AMD was put into the jar and periodically shaken vigorously.

The most obvious result was that the iron in the AMD precipitated quite rapidly in the form of iron hydroxide. This was probably due to the high pH of the gel material. The supernatant solutions were periodically analyzed to see the effect on the AMD composition. Table XV shows the results of such an analysis made after 10 days. It can be seen that the presence of the gel caused most of the acidic constituents of the AMD to be precipitated out of solution.

Table XV. Analysis of Supernatant AMD in Gel Stability Tests

	Analysis of AMD	AMD + Silica/ Alumina (Shaken)	AMD + Silica/ Alumina (Without Shaking)
pH	2.3	8.5	4.5
Acidity on $CaCO_3$, ppm	3950	—	180
Total dissolved iron	1117	5	110
Ferrous	120	—	0
Sulfate	3260	760	1330
Soluble silica	0	200	80

The gel itself did not appear to be affected in any way, although it was hard to see if there was any change in the shaken test. The gel mass was covered with yellowish-brown iron hydroxide which might have masked any erosion.

ANALYSIS OF BACTERIA CONTENT OF WASH EFFLUENT

A sample of the wash effluent from the control pile (pile A) was taken after about 100 in. of equivalent rainfall had passed through the pile. This sample was analyzed for bacteria content under the direction of Dr. Harold L. Lovell of Pennsylvania State University. The analysis shows a bacteria count of 2.4×10^4 cells/ml* as compared to an average cell count of about 100 in the effluent from a coal mine.[9] The cell concentration in effluents from existing refuse piles is probably somewhat higher than that of the coal mine effluent, but an exact value is not available at this writing.

The very high cell count in the effluent from the control pile washing helps explain the fact that almost all the effluent solutions showed very high ferric and very low ferrous concentrations. It has been shown[9,10] that bacteria in acid solutions promote the oxidation of ferrous ion with the rate of oxidation varying directly with the bacteria concentration. Thus the fact that the effluent from the laboratory piles shows abnormally high bacteria counts is consistent with the very high ferric concentrations.

The reasons for the abnormally high bacteria count are hard to determine in the absence of controlled experimentation, but the environmental conditions were certainly conducive to the propagation of biological organisms. The refuse was kept in a highly humid atmosphere at temperatures consistantly above 60 °F and the pyrite content was relatively high. These conditions undoubtedly encouraged the growth of the microorganisms and the resulting ferrous oxidation.

---

*This value was obtained by a dilution count procedure developed at Penn. State University by Stone, Tieman and Lovell.[9]

BLANK PAGE

SECTION 10

MASS BALANCE

METHOD

The major soluble species in an acidic mine water include ferrous iron, ferric iron, sulfate, water, hydroxyl, and hydrogen ions. These materials do not exist solely as the bare ions but, in part, as complex ions, e.g., $[Fe_2(OH)_2]^{4+}$, $FeOH^{2+}$, $Fe(OH)_2^{+}$, etc. Since these ions control the chemistry of AMD waters, an understanding of their distribution as a function of gross solution composition is required. There is also the more subtle point that a mass balance is required as a check on the thoroughness and accuracy of the analysis. A "natural" system such as AMD is generally quite complex but, more important, variable in composition. The self-consistency of results provides some confidence that all major species have been accounted for. As will be seen from the data, some analytical procedures had to be modified.

The equilibria among the ferric, ferrous, sulfate, hydroxyl, and hydrogen species are summarized in Table XVI . The equilibrium constants used are shown in Table XVII.

Table XVI . Equilibrium Between Fe^{3+}, Fe^{2+}, OH^-, SO_4^{2-}

Equilibrium Reactions	Equilibrium Expression
$2\ Fe^{3+} + 2\ H_2O = Fe_2(OH)_2^{4+}$	$K_{22} = \frac{[Fe_2(OH)_2^{4+}]\ [H^+]^2}{[Fe^{3+}]^2}$
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	$K_{11} = \frac{[FeOH^{2+}]\ [H^+]}{[Fe^{3+}]}$
$Fe^{3+} + H_2O = Fe(OH)_2^{+} + 2\ H^+$	$K_{12} = \frac{[Fe(OH)_2^{+}]\ [H^+]^2}{[Fe^{3+}]}$
$Fe^{3+} + SO_4^{2-} = FeSO_4^{+}$	$K_{01} = \frac{[FeSO_4^{+}]}{[Fe^{3+}]\ [SO_4^{2-}]}$

Table XVI. (Cont.)

Equilibrium Reactions	Equilibrium Expression
$Fe^{3+} + 2\ SO_4^{2-} = Fe\ (SO_4)_2^-$	$K_{02} = \dfrac{[\ Fe\ (SO_4)_2^-]}{[\ Fe^{3+}]\ [\ SO_4^{2-}]^2}$
$SO_4^{2-} + H^+ = HSO_4^-$	$K_{00} = \dfrac{[\ HSO_4^-]}{[\ SO_4^{2-}]\ [\ H^+]}$
$Fe^{2+} + SO_4^{2-} = FeSO_4$	$Q_{01} = \dfrac{[\ FeSO_4]}{[\ Fe^{2+}]\ [\ SO_4^{2-}]}$
$Fe^{2+} + H_2O = Fe(OH)^+ + H^+$	$Q_{11} = \dfrac{[\ Fe(OH)^+]\ [\ H^+]}{[\ Fe^{2+}]}$

Table XVII. Log Equilibrium Constants* for Fe^{3+}, Fe^{2+}, OH^-, SO_4^{2-} Species

Constant	Value
K_{22}	−2.91
K_{11}	−3.05
K_{12}	−6.31
K_{01}	+2.31
K_{02}	+2.62
K_{00}	+2.00
Q_{01}	+0.23
Q_{11}	−6.74

---

* Taken from L. G. Sillen, A. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

These constants, particularly K_{22} and K_{11}, are all functions of ionic strength, i.e., the total ion concentration. This dependence remains to be determined experimentally and is considered as an area of theory refinement.

In addition to the eight equilibria in Table XVI, there are mass balances on Fe(II), Fe(III), SO_4^{2-}, and H^+ to be satisfied:

$$C_{Fe(II)} = [Fe^{2+}] + [FeSO_4] + [FeOH^+] \tag{8}$$

$$\begin{aligned} C_{Fe(III)} = {} & [Fe^{3+}] + [FeSO_4^{\ +}] + [Fe(SO_4)_2^{\ -}] + [FeOH^{2+}] \\ & + [Fe(OH)_2^{\ +}] + 2\,[Fe_2(OH)_2^{\ 4+}] \end{aligned} \tag{9}$$

$$C_S = [SO_4^{2-}] + [HSO_4^-] + [FeSO_4] + [FeSO_4^+] + 2\,[Fe(SO_4)_2^-] \tag{10}$$

$$\begin{aligned} C_H = {} & 2\,C_S - 2\,C_{Fe(II)} - 3\,C_{Fe(III)} \\ = {} & [H^+] + [HSO_4^-] - [OH^-] - [FeOH^+] - [FeOH^{2+}] \\ & - 2\,[Fe(OH)_2^{\ +}] - 2\,[Fe_2(OH)_2^{\ 4+}] \end{aligned} \tag{11}$$

The method of solution consists of the following steps, which comprise part 2 of the computer program in Table XVIII.

First, the equilibria constants are substituted to eliminate all species except $[Fe^{2+}]$, $[Fe^{3+}]$, $[SO_4^{\ 2-}]$, and $[H^+]$, which are the master variables. The four mass balances (Eqs. 8 through 11) then provide four equations in these four unknowns, provided that all the total concentrations are known. These are rearranged as follows:

$$[Fe^{2+}] = \frac{C_{Fe(II)}}{1 + Q_{01}\,[SO_4^{\ 2-}] + \dfrac{Q_{11}}{[H^+]}} \tag{12}$$

$$[Fe^{3+}] = C_{Fe(III)} \Bigg/ \left(1 + K_{01}[SO_4^{\ 2-}]^2 + K_{02}\,(SO_4^{\ 2-})^2 + \frac{K_{11}}{[H^+]} + \frac{K_{12}}{[H^+]^2} + \frac{2\,K_{22}\,[Fe^{3+}]}{[H^+]^2}\right) \tag{13}$$

Table XVIII. Computer Printout

```
1.01\  PROGRAM /FE2/   JNB-RJJ   VERSION 3/3/70
1.1 TYPE"

        FE(II) AND FE(III) IN SULFATE, INCLUDING ACIDITY

"
1.14 DEMAND IN FORM 1: CFE, CF2, CS
1.141 CFE = .00002 IF CFE = 0
1.142 CF2 = .00001 IF CF2 = 0
1.145 CF3 = (CFE - CF2)/55.85, CF2=CF2/55.85, CS = CS/96.06
1.15  TYPE IN FORM 2: CF2, CF3, CS
1.2 CF2 = CF2*.001, CF3 = CF3*.001, CS=CS*.001
1.21 FE = 0.2*CF3, SO4 = 0.5*CS, H = .003, CH = 2*CS-2*CF2-3*CF3
1.22 TYPE "NEGATIVE ACIDITY" IF CH<0
1.23 TYPE CH IF CH<0
1.24 DEMAND CH IF CH<0
1.25  K22 = 10^-2.91, K11 = 10^-3.05, K12 = 10^-6.31,
      K01 = 10^2.31, K02 = 10^2.62, Q01 = 10^.23, Q11=10^-6.74
1.29 TYPE"
   PH    FE+3    SO4   FE2(OH)2  FEOH  FE(OH)2   FESO4  FE(SO4)2 FE++"
 1.3 TO PART 2
2.05 FEN = FE, SON = SO4
2.08 F2 = CF2/(1+Q01*SO4+Q11/H)
2.1 FE = CF3/(K01*SO4 + K02*SO4^2 + 1 + 2* K22*FE/H^2 +
               K12/H^2 + K11/H)
2.2 SO4 = CS/(1 +  K01*FE +2*K02*FE*SO4+Q01*F2+100*H)
2.3 A1 = 10^-14+Q11*F2+K11*FE,  A2= 2*FE*(K12 +K22*FE),
     A3 = 1+100*SO4
2.35 F = CH + A1/H + A2/H^2 - A3*H
2.4 FPR = -(A1/H^2 + 2*A2/H^3 + A3)
2.5 HN = H - F/FPR
2.6 TO STEP 2.7 IF ABS( 1 - H/HN) <10^-7
2.65 H = HN
2.67 TO STEP 2.05
2.7 TO STEP 2.8 IF ABS(1-FEN/FE) < 10^-7
2.75 TO STEP 2.05
2.8 TO STEP 2.9 IF ABS (1-SON/SO4) <10^-7
2.85 TO STEP 2.05
2.9 TO PART 3
3.2 PH = -LOG10(H), C22 = K22*FE^2/H^2, C11 = K11*FE/H,
      C12 = K12*FE/H^2, C01 = K01*FE*SO4, C02 = K02*FE*SO4^2
3.25 FE = 1000*FE, SO4 = 1000*SO4, C22 = 1000*C22, C11 = 1000*C11,
     C12 = 1000*C12, C01 = 1000*C01, C02 = 1000*C02, F2 = 1000*F2
3.3 TYPE IN FORM 3: PH, FE, SO4, C22, C11, C12, C01, C02, F2
3.4 CHM = CH*1000, CHP = CHM*50.04, CHT =(CH+2*CF2+3*CF3)*1000,
     CPP = CHT*50.04
3.42 TYPE IN FORM 4: CHM, CHP, CHT, CPP
3.45 LINE FOR L = 1,2
3.5 TO STEP 1.14
```

Table XVIII. (Cont.)

```
FORM 1:
          PPM FE TOTAL = #,   PPM FE(II) = #,   PPM SO4 = #
FORM 2:
                    TOTAL FE(II)  = ZZZ.ZZZ MM
                    TOTAL FE(III) = ZZZ.ZZZ MM
                    TOTAL SO4     = ZZZ.ZZZ MM
FORM 3:
 ZZ.ZZ ZZZ.ZZZ ZZZ.ZZZ ZZZ.ZZZ ZZZ.ZZZ ZZZ.ZZZ ZZZ.ZZZ ZZZ.ZZZ ZZZ.ZZZ
 FORM 4:
       EXCESS ACIDITY = ZZZ.ZZZ MM, ZZZZZZ PPM CACO3
        TOTAL ACIDITY = ZZZ.ZZZ MM, ZZZZZZ PPM CACO3
```

This program is written in CAL, the conversational algebraic language of the XDS-940 time-sharing computer system. Part 1 is input, Part 2 is calculation, and Part 3 is output. Symbols are defined as follows:

CFE	Total iron in ppm (redefined to millimolar in 1.145)
CF2	Ferrous iron in ppm "
CS	Total sulfate in ppm "
CF3	Ferric iron in millimolar
	Note concentrations are redefined to molar in 1.2
FE	free ferric iron, molar
SO4	free sulfate, molar
H	free hydrogen ion, molar
CH	total acidity, molar, due to excess acid
K22	formation constant for $Fe_2(OH)_2^{4+}$ from Fe^{3+} and H^+
K11	" $FeOH^{++}$ "
K12	" $Fe(OH)_2^+$ "
K01	" $FeSO_4^+$ " and $SO_4^=$
K02	" $Fe(SO_4)^-$ " "
Q01	" $FeSO_4$ from Fe^{++} "
Q11	" $FeOH^+$ " and H^+
FEN	new value of FE in iteration
SON	new value of SO_4 in iteration
A1, A2, A3, F, FPR, etc.	intermediate results defined by equations in the program
C22, C21, etc.	concentration of complexes corresponding to K22, etc. recalculated to millimolar in step 3.25.
CHM	total acidity, millimolar, due to excess acid
CHP	total acidity, ppm $CaCO_3$, due to excess acid
CHT	total acidity, millimolar, due to acid plus iron species
CPP	total acidity, ppm $CaCO_3$, due to acid plus iron species

Note that no account has been taken of variations in activity coefficient or the possibility of precipitate ($Fe(OH)_3$?) formation.

$$[SO_4^{2-}] = C_S \bigg/ \left(1 + K_{01} [Fe^{3+}] + 2 K_{02} [Fe^{3+}] [SO_4^{2-}] + Q_{01} [Fe^{2+}] + K_{00} [H^+]\right) \quad (14)$$

$$F(H) = O = C_H + \frac{A_1}{[H^+]} + \frac{A_2}{[H^+]^2} - A_3 [H^+] \quad (15)$$

where

$$A_1 = 10^{-14} + Q_{11} [Fe^{2+}] + K_{11} [Fe^{3+}]$$

$$A_2 = 2 [Fe^{3+}] (K_{12} + K_{22} [Fe^{3+}])$$

$$A_3 = 1 + K_{00} [SO_4^{2-}]$$

Second, the equations are solved by an iterative procedure. $[Fe^{3+}]$ is assumed initially to be 0.2 $C_{Fe(III)}$, $[SO_4^{2-}]$ is assumed initially to be 0.5 C_S, and $[H^+]$ is assumed initially to be 0.003M. These are merely starting values and are not critical. The closer they are to the final values the faster the equations will converge, but the exact values should not influence the final answer.

Then, $[Fe^{2+}]$, $[Fe^{3+}]$, and $[SO_4^{2-}]$ are evaluated from Eqs. (12) to (14), and the polynomial in H^+ (Eq. 15) is solved using Newton's method. These revised values are then used in a further evaluation of the master variables using the same set of equations. When two successive sets of values converge to one part in 10^7, the calculation is complete. Normally, this requires only a few iterations, since the equations have been arranged so that the revised values make very little change in the master variables when they are recomputed. The manner in which the equations are rearranged and the order in which they are evaluated is quite critical in obtaining a rapid solution — in some of our earlier attempts, a different rearrangement of Eq. (10) (substractive rather than divisive) did not give convergence in solutions which were high in iron content.

The input data then are the total soluble iron content, soluble ferrous iron, and soluble sulfate. The output (Table XIX) is a display of the individual complex ion concentrations as well as predictions of pH and total acidity. The correspondence of experimentally determined and predicted pH and total acidity is a measure of the internal consistency of the theory.

An additional value obtainable from the mass balance is the free acidity, i.e., the amount of sulfuric acid not involved with soluble metal ion complexes. In principle, this should be directly computable from pH. The pH electrode measures the negative log of the hydrogen ion activity ($-\log A_{H^+}$), not concentration. The activity is a function of a number of factors such as ionic strength. An approximate correction for this factor was included in the computer program. The "predicted" free acidity does not involve this

Table XIX. Sample Output

```
ACID MINE WATERS 3/13/70 JNB      PAGE 1

>LOAD
 FROM /@FE2/
>DO PART 1


          FE(II) AND FE(III) IN SULFATE, INCLUDING ACIDITY


           PPM FE TOTAL = 275,   PPM FE(II) = 15,  PPM SO4 = 560

                  TOTAL FE(II)  =    0.269 MM
                  TOTAL FE(III) =    4.655 MM
                  TOTAL SO4     =    5.830 MM
NEGATIVE ACIDITY
      CH =          -2.8437538E-03
    CH  = 0

   PH    FE+3    SO4   FE2(OH)2  FEOH  FE(OH)2   FESO4  FE(SO4)2 FE++
   2.76  1.314   4.024   0.689   0.667  0.209   1.079   0.009   0.267
       EXCESS ACIDITY =   0.000 MM,     0 PPM CACO3
       TOTAL ACIDITY =  14.503 MM,    726 PPM CACO3

           PPM FE TOTAL = 275,   PPM FE(II) = 15,  PPM SO4 = 720

                  TOTAL FE(II)  =    0.269 MM
                  TOTAL FE(III) =    4.655 MM
                  TOTAL SO4     =    7.495 MM

   PH    FE+3    SO4   FE2(OH)2  FEOH  FE(OH)2   FESO4  FE(SO4)2 FE++
   2.75  1.262   5.196   0.610   0.628  0.193   1.338   0.014   0.266
       EXCESS ACIDITY =   0.487 MM,     24 PPM CACO3
       TOTAL ACIDITY =  14.991 MM,    750 PPM CACO3

           PPM FE TOTAL = 1195,   PPM FE(II) = 0,  PPM SO4 = 3745

                  TOTAL FE(II)  =    0.000 MM
                  TOTAL FE(III) =   21.397 MM
                  TOTAL SO4     =   38.986 MM

   PH    FE+3    SO4   FE2(OH)2  FEOH  FE(OH)2   FESO4  FE(SO4)2 FE++
   2.19  4.764  14.562   0.668   0.657  0.056  14.164   0.421   0.000
       EXCESS ACIDITY =  13.782 MM,    690 PPM CACO3
       TOTAL ACIDITY =  77.972 MM,   3902 PPM CACO3
```

activity problem and, once a complete mass balance is obtained, should provide a more accurate evaluation of the free acid to be treated.

APPLICATION TO STANDARD SAMPLES

The program was first checked out with simple sulfuric acid solutions containing known amounts of ferric and ferrous sulfate. A comparison of known, measured, and predicted parameters is shown in Table XX The known and predicted acidities compared to within 5%; the titrated values generally tend to be low, by about 6% on the average.

Table XXI shows the distribution of the various complex iron species, as predicted by the equilibrium constants of Table XVI . The dominant ferrous iron species is Fe^{2+} while, depending on pH, the principle ferric iron species are the $Fe(SO_4)^+$ complex and the bare Fe^{3+}. Note that the amount of ferric iron present as hydroxyl complexes is a pronounced function of pH; a pH change of 2.58 to 1.8 lowers the concentration of $Fe_2(OH)_2^{2+}$ from 10.6 to 0.72%.

APPLICATION TO AMD SAMPLES

The mass balance equations were then applied to AMD waters, generated in the manner described. A large number of evaluations were made. The data given below (Table XXII) are representative of the results.

Consider the ten samples listed in Table XXII. For a number of samples, e.g., 1, 3, 4, 7, 8, 9, the agreement is reasonable. However, the remaining samples show pronounced discrepancies; in all cases, the measured acidities are higher than predicted. This is what could be expected if another anion, besides sulfate, was present. A likely possibility from the AMD generation mechanism is sulfite (SO_3^{2-}). Indeed, as mentioned, oxidizing the solution before titration did, in some cases, lead to additional sulfate. Sulfurous acid is titratable to a phenolphthalein end point, and would therefore contribute to the measured acidity and pH.

The data for samples 10, 9, 7, and 6 were remeasured on this basis. The results are shown in Table XXIII.

Table XX. Comparison of Parameters for Standard Samples

Sample	Composition	pH		Total Acidity (ppm $CaCO_3$)		
		Measured	Predicted	Known	Measured	Predicted
1	H_2SO_4	1.95	1.84	1020	1000	1021
2	$FeSO_4$ (1050 ppm Fe)	4.9	4.5	1870	1840	1882
3	$FeSO_4$ (1050 ppm Fe) in H_2SO_4 (1000 ppm)	2.25	2.0	2870	2800	2903
4	$Fe_2(SO_4)_3$ (1050 ppm) in H_2O	2.2	2.58	2210	2600	2864
5	$Fe_2(SO_4)_3$ (737 ppm) in H_2O	2.7	2.64	1870	1900	1982
6	$Fe_2(SO_4)_3$ (1050 ppm) in H_2SO_4 (1000 ppm)	2.1	2.01	3870	3600	3885
7	$Fe_2(SO_4)_3$ (737 ppm) in H_2SO_4 (1000 ppm)	2.5	2.0	2950	2650	3000
8	Fe (1950 ppm) + H_2SO_4	1.5	1.8	—	7306	7451

Table XXI. Relative Amounts of Soluble Iron Species (Mol % Total Fe)

Sample	Fe^{2+}	$Fe_2(OH)_2{}^{4+}$	$Fe(OH)^{2+}$	$Fe(OH)_2{}^{+}$	$Fe(SO_4)^{+}$	$Fe(SO_4)_2{}^{-}$	Fe^{2+}	pH (Calc.)
2							99.1	4.5
3							98.9	2.0
4	17.7	10.6	6.0	1.3	52.3	1.5	—	2.58
5	25.4	1.6	2.3	0.13	67.2	1.8	—	2.01
6	20.3	0.72	1.13	0.04	74.4	2.73	—	1.8

Table XXII. Typical AMD Samples

Sample No.	pH		Acidity		Total Fe, ppm	Ferrous Iron, ppm	Sulfate, ppm
	Measured	Predicted	Measured	Predicted			
1	2.5	2.30	3950	3396	1117	120	3260
2	2.4	2.42	5705	3909	1370	110	3752
3	2.7	2.2	3150	2969	880	88	2850
4	2.7	2.22	3230	3162	980	90	3035
5	2.5	2.6	4200	3269	1306	270	2850
6	2.05	2.54	5505	4849	1804	—	4315
7	2.2	2.38	2803	2657	871	—	2550
8	2.1	2.19	3904	3902	1195	—	3745
9	2.1	2.43	4153	3820	1324	—	3669
10	2.5	2.58	3353	2763	1028	—	2471

Table XXIII. AMD Samples Corrected for Sulfate

Sample No.	pH		Acidity			SO_4^{2-}
	Measured	Predicted	Measured	Predicted	SO_4^{2-}	$+SO_3^{2-}$
6	2.05	2.25	5505	5518	4315	5296
7	2.2	2.28	2803	2810	2550	2697
9	2.1	2.28	4153	4087	3667	3923
10	2.5	2.2	3353	3426	2471	3288

Judging from the results, this approach to the mass balance problem appears to be valid. One important result of this analysis was the definition of a soluble "reduced sulfate." It is equally apparent that further refinement is necessary, in particular to add to the computer program a subroutine which accounts for the deviations of the activity coefficients from unity. It will also be necessary to account for the contributions from soluble calcium and aluminum species.

SECTION 11

REFERENCES

1. Vanderhoof, R. A., "Stream Pollution by Coal Mine Drainage in Appalachia," U. S. Department of the Interior, FWPCA, Cincinnati, Ohio (1967, rev. 1969).

2. Peters, J. W., Spicer, P. S., Lovell, H. L., Special Report SR-67, Pennsylvania State University to Coal Research Board, Commonwealth of Pennsylvania (January 1968).

3. Waksman, S. A. and Joffe, S. S., Science, 53, 216 (1921).

4. Ashmead, D., Colliery Guardian, 190, 694-8 (1955).

5. McGoran, C. J. M., Duncan, D.W., and Walden, C. C., Canadian J. Microbiol. 15(1), 135-8 (1969).

6. Hill, R. "Mine Drainage Treatment — State of the Art and Research Needs," U. S. Department of the Interior, FWQA, Cincinnati, Ohio (December 1968), p. 8.

7. Vail, J. G., "Soluble Silicates," Vol. 1, Chapter 5, Reinhold Pub. Corp., New York, 1952.

8. "Acid Mine Drainage in Appalachia," Regional Commission, 1969.

9. Lovell, H. L., private communication based on unpublished research under FWQA project # WPRD-34-01-68.

10. Glover, H. G., presented at the 22nd Annual Purdue Ind. Waste Conf., May 1967. "The Control of Acid Mine Drainage Pollution by Biochemical Oxidation and Limestone Neutralization Treatment," May 1967.

SECTION 12

PUBLICATIONS

A presentation of much of the data included in this document was made at the Third Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., May 19, 1970 in the paper "Presentation of Acid Mine Drainage: Silicate Treatment of Coal Mine Refuses Piles" by Arthur Walitt, Raymond Jasinski, and Bertram Keilin.

APPENDIX I

ANALYTICAL METHODS

The parameters determined routinely were pH, acidity (calcium carbonate), total soluble iron, ferrous iron, and sulfate. Determinations of aluminum and calcium were made on selected samples. The analytical methods were based on those given in: "Standard Methods for the Examination of Water and Waste Water, " 12th ed., American Public Health Association, New York (1965).

pH was measured with a standard Beckman pH meter calibrated at pH 2 with standard buffer solution. It was found that standardization at pH 6 introduced an error of 0.2 unit at pH 2.

Total iron was determined, after filtering the sample, by first reducing with $SnCl_2$ solution followed by destruction of the excess $SnCl_2$ with $HgCl_2$, followed by titration with dichromate using diphenylamine sulfonate as the indicator. The accuracy of the method was proven by titrating standard ferric and ferrous sulfate solutions.

Ferrous iron was measured by direct titrations with dichromate using diphenylamine sulfonate as an indicator.

Total acidity was measured by titration of the untreated solution at room temperature to a phenolphthalein end point. This value therefore includes the free acid as well as the resulting from the hydrolysis of soluble iron. Data are reported in terms of the equivalent ppm calcium carbonate.

Sulfate was determined primarily by precipitation with benzidine hydrochloride followed by titration of the released HCl with sodium hydroxide to the phenolphthalein end point. This method is rapid, although apparently less accurate than the standard gravimetric barium sulfate technique. Table I shows the sulfate analysis by the two techniques.

Neither of the two methods necessarily gave total soluble sulfur content. It was found that, depending on the specific AMD sample, a reduced sulfate, presumably sulfite ion, was often present. The addition of bromine water was sufficient to oxidize this material. The results of the sulfate analysis with and without this pretreatment are shown in Table II.

Table XXIV. Sulfate Analysis, ppm

Sample	Benzidine HCl	Gravimetric	Gravimetric, B-HCl
1	2430	2481	1.015
2	3230	3288	1.015
3	38,060	38,602 *	1.014
4	3568	3745	1.05

---

* Standard known amount 39,100 ppm.

Table XXV. Sulfate Analysis (PPM) With and Without Preoxidation

Sample	As Received	After Oxidation	After Oxid., As Received
1	2430	3220	1.33
2	3667	3923	1.07
3	4315	5296	1.23
4	2550	2697	1.06
5	445	480	1.08
6	285	290	1.02
7	405	405	0.0

As can be seen, the ratio of the two "sulfates" varies from sample to sample, even though the AMD samples all came from the same pile of waste coal refuse.

Soluble silica was determined as molybdenum blue by reduction of a preformed yellow silico-molybdate complex. This complex is formed as the acid at a pH of 1.6. After its reduction to the molybdenum blue, the concentration of the sample is determined by comparison with a standard silica color disk.

COMPLETE ANALYSIS OF PILE EFFLUENTS

Table XXVI. Pile A: Control

Day*	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
1†	20	1.8	32,629	6134	1586	14,272	0
		2.05	16,114	2837	739	11,893	0
2†	20	2.0	20,500	5250	614	11,800	0
		2.15	14,160	2620	430	4,738	0
6	40	2.0	18,100	3860	490	7,457	0
7	20	2.0	15,600	2569	167	7,136	0
8	100	2.3	6,265	1787	90	6,660	0
10	50	2.4	4,604	1117	60	4,281	0
13	50	2.05	10,000	2624	112	7,612	0
14	1	2.15	8,670	3871	390	9,500	0
16	50	2.1	9,350	3518	130	5,327	0
23	20	1.8	16,220	4300	580	8,270	0
	100	2.3	4,360	1210	110	4,370	0
24	100	2.5	3,150	980	90	3,950	0
27	100	2.3	3,950	1117	120	3,260	0
28	100	2.2	3,460	1284	112	2,660	0
29	100	2.3	3,200	950	90	1,940	0
30	100	2.3	3,353	1040	90	2,280	0
31	100	2.5	3,250	940	80	2,280	0

---

*The data are grouped by weeks, with the day numbers indicating time elapsed from the start of the experiment.

†On days 1 and 2, the pile effluent was separated into the inner core sample and the outer annulus sample. The top figure for each day is the inner sample. Data for all other days refer to composite samples which reflect the average composition of the total wash volume.

Table XXVI. (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
34‡	2	2.2	5,105	1370	110	3,752	0
	80	2.3	4,030	950	85	3,230	0
35	100	2.5	3,150	880	88	2,850	0
36	100	2.5	3,230	980	90	3,035	0
37	100	2.5	3,280	1009	100	2,204	0
43	60	2.0	5,060	2680	366	4,180	0
44	100	2.3	4,430	1843	290	3,270	0
45	100	2.3	4,200	1306	270	2,850	0
48	100	2.3	3,700	1360	245	2,480	0
49	100	2.5	2,960	970	210	2,000	0
50	100	2.5	2,350	840	160	1,780	0
52	100	2.5	2,220	780	100	1,560	0
55	100	2.3	2,260	715	90	1,350	0
56	100	2.5	1,950	650	80	1,280	0
57	100	2.5	1,890	630	70	1,180	0
58	100	2.3	2,040	715	85	1,230	0
59	100	2.3	1,980	760	90	1,190	0
62	100	2.3	1,900	730	60	1,045	0
63	100	2.4	1,770	680	60	960	0
64	100	2.5	1,400	510	45	870	0
65	100	2.55	1,000	460	38	740	0
66	100	2.6	670	340	20	665	0

---

‡On day 34, the top figures are the analysis of the first 2-ℓ wash; the other figures are the analysis of the composite samples.

Table XXVI. (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
69	100	2.4	1,210	360	25	650	0
70	100	2.6	630	310	20	580	0
71	100	2.6	540	278	18	545	0
72	100	2.6	510	250	15	470	0
73	100	2.6	530	240	15	450	0
76	100	2.4	560	290	20	490	0
77	100	2.6	490	210	15	430	0
78	40	2.4	550	320	25	580	0
83	100	2.3	750	430	40	640	0
84	100	2.6	410	210	12	380	0
85	100	2.6	390	160	10	230	0
87	100	2.65	375	150	8	210	0
90	100	2.5	510	190	10	420	0
91	100	2.65	350	150	10	230	0
92	100	2.6	420	150	10	275	0
93	100	2.6	380	130	10	240	0
94	100	2.65	330	130	8	200	0
97	100	2.6	400	140	5	230	0
98	100	2.65	290	110	0	190	0
99	100	2.6	260	80	0	190	0
100	100	2.6	240	66	0	170	0
101	100	2.7	250	56	0	150	0
104	100	2.5	360	110	8	220	0
105	100	2.7	250	80	0	190	0
106	100	2.8	200	66	0	170	0
107	100	2.8	230	56	0	190	0
108	100	2.8	200	56	0	190	0
111	100	2.7	270	80	0	230	0
112	100	2.7	240	66	0	220	0
113	100	2.7	200	60	0	190	0
114	100	2.7	200	70	0	240	0
115	100	2.7	240	80	0	230	0

Table XXVI. (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
118	100	2.6	250	90	0	250	0
119	100	2.8	200	80	0	190	0
120	100	2.6	230	82	0	210	0
121	100	2.7	250	80	0	290	0
122	100	2.6	300	60	0	300	0
125	100	2.5	320	95	0	330	0
126	100	2.6	290	72	0	290	0
127	100	2.6	270	65	0	290	0
128	100	2.5	310	72	0	290	0
129	100	2.6	250	55	0	240	0
139	100	2.1	530	275	0	460	0
140	100	2.2	280	95	0	260	0
141	100	2.4	210	65	0	185	0
142	100	2.4	260	80	0	240	0
143	100	2.5	280	80	0	265	0
146	100	2.4	350	95	0	320	0
147	100	2.5	240	80	0	220	0
148	100	2.5	200	70	0	190	0
149	100	2.5	210	70	0	190	0
150	100	2.5	190	65	0	185	0
153	100	2.2	260	90	0	205	0
154	100	2.4	220	75	0	195	0
155	100	2.4	200	80	0	190	0
156	100	2.5	190	80	0	190	0
157	100	2.5	180	70	0	170	0
160	100	2.4	220	90	0	200	0
161	100	2.6	180	60	0	165	0
162	100	2.6	170	60	0	165	0
163	100	2.7	150	55	0	140	0
164	100	2.7	150	60	0	145	0
167	100	2.5	190	75	0	170	0
168	100	2.6	160	60	0	155	0
169	100	2.6	160	70	0	150	0

Table XXVI. (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
170	100	2.6	180	80	0	170	0
171	100	2.7	150	50	0	140	0
174	100	2.6	210	100	0	200	0
175	100	2.6	200	80	0	185	0
176	100	2.7	200	80	0	190	0
177	100	2.7	180	70	0	170	0
178	100	2.7	160	60	0	150	0
181	100	2.6	190	70	0	170	0
182	100	2.7	160	50	0	150	0
183	100	2.7	150	50	0	150	0
184	100	2.8	130	50	0	120	0
185	100	2.8	130	40	0	130	0
188	100	2.6	170	65	0	150	0
189	100	2.8	150	60	0	150	0
190	100	2.8	140	50	0	140	0

Table XXVII. Pile B: Neutralized Pile

Day*	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm†	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
1	20	2.4	11,510	3462	726	7136	—
2	20	10.5	—	73	—	2854	—
3	20	5.5	1000	390	45	1500	—
6	20	10.3	—	50	—	960	—
7	20	10.1	—	12	—	475	400
8	100	9.8	—	40	—	1283	350
10	50	9.3	—	17	—	1903	320
13	50	9.5	—	16	—	1410	400
14	20	8.6	—	44	—	1820	320
16†	50	8.8	—	39	—	1638	230
		8.3	—	42	—	1120	160
20 ‡	50	7.6	—	11	—	1615	160
		6.8	—	11	—	1140	90
21	50	6.8	—	11	—	1320	110
22	50	7.0	—	11	—	980	120
23	100	6.8	—	11	—	730	100
24	100	6.5	—	11	—	680	100
27	100	6.5	—	15	—	360	80
28	100	6.5	—	11	—	380	60
29	100	6.5	—	27	—	320	60
30	100	6.5	—	15	—	285	70
31	100	6.5	—	11	—	285	60
34	100	6.5	—	22	—	190	70
35	100	6.5	—	27	—	190	60
36	100	6.5	—	33	—	130	60
37	100	6.5	—	28	—	100	40

---

*Pile was treated on days 0, 1, and 3 until the effluent stream had the same pH as the fresh silicate solution.

†Includes finely suspended iron hydroxide.

‡On days 16 and 20, the first and last 2 ℓ only of the 50-ℓ total were analyzed and reported. For material balances, the composite analysis was estimated as the average of these two figures.

Table XXVII. (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
43	60	3.5	420	45	13	290	80
44	100	3.5	395	52	13	355	30
45	100	3.0	450	61	16	380	30
48*	100	2.8	650	85	10	420	60
		3.0	570	100	15	360	50
49	100	3.0	480	90	15	475	20

---

*On day 48, the top figures are the analysis of a sample collected from the inner core, while the other sample, on the same day, was collected from the outer annulus.

Table XXVIII. Pile C: Silica Gel (Surface Treatment)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm*	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
1	20	10.1	—	112	—	475	100
2	100	6.8	10	89	—	475	100
3	50	8.3	—	22	—	727	110
6	50	9.1	—	16	—	390	120
7	20	9.3	—	122	—	780	140
9†	50	9.5	—	182	—	833	140
		9.0	—	82	—	583	80
13†	50	8.7	—	25	—	920	80
		7.2	—	15	—	640	60
14	50	6.8	—	15	—	760	70
15	50	6.5	—	11	—	690	60
16	100	6.5	—	15	—	615	60
17	100	6.5	—	22	—	680	70
20	100	6.3	—	39	—	530	60
21	100	6.3	—	44	—	340	50
22	100	6.5	—	27	—	280	40
23	100	6.3	—	22	—	285	34
24	100	6.3	—	22	—	190	30
27	100	6.5	—	17	—	150	40
		6.5	—	15	—	130	40
28	100	6.5	—	22	—	130	40
29	100	6.5	—	28	—	140	50
30	100	6.5	—	40	—	130	40
36‡	60	6.5	—	50	—	180	60
37	100	3.0	815	180	30	1045	90
38	100	2.8	850	245	56	975	90

---

*Includes finely suspended iron hydroxide.

†On days 9 and 13, only the first and last 2 ℓ of the 50-ℓ total wash were analyzed.

‡On day 36, the pile was vigorously disturbed to test the effect of shifts in the refuse pile structure.

Table XXVIII. (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
41	100	2.8	780	265	48	860	70
42	100	3.0	630	230	45	780	60
43	100	3.0	690	250	40	810	80
45	100	3.0	650	270	30	780	60
48	100	2.9	830	250	20	540	50
49	100	3.0	720	230	13	420	50
50	100	3.2	580	200	11	380	40
51	100	3.0	760	220	11	420	40
52	100	3.0	830	230	13	440	40
55	100	2.9	880	270	15	400	45
56	100	2.9	770	212	10	360	40
57	100	2.8	820	201	10	280	30
58	100	2.8	790	201	10	285	30
59	100	2.8	730	170	8	230	20
62	100	2.7	770	190	10	290	25
63	100	2.8	510	110	8	215	20
64	100	2.8	480	78	6	180	20
65	100	2.8	460	72	5	180	20
66	100	2.8	430	78	5	160	20
69	100	2.6	470	85	5	170	10
70	100	2.8	350	80	5	120	10
71	40	2.7	380	95	8	160	12
76	100	2.6	450	130	15	180	15
77	100	2.8	320	80	5	110	8
78	100	2.8	205	56	0	95	6
80	100	2.9	190	56	0	90	6
83	100	2.9	200	60	0	100	8
84	100	2.9	190	56	0	90	5
85	100	2.9	210	66	0	110	6
86	100	2.8	230	66	0	130	4
87	100	2.9	240	50	0	130	4

Table XXVIII. (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
90	100	2.8	240	80	0	160	8
91	100	2.9	200	66	0	110	4
92	100	2.9	180	56	0	95	2
93	100	2.9	150	50	0	80	2
94	100	2.9	170	56	0	120	4
97	100	2.8	190	80	0	160	6
98	100	2.8	160	66	0	140	4
99	100	2.7	180	72	0	110	4
100	100	2.7	180	80	0	110	6
101	100	2.7	160	66	0	95	2
104	100	2.6	240	115	0	190	8
105	100	2.6	260	90	0	190	6
106	100	2.6	220	110	0	160	6
107	100	2.7	250	90	0	170	4
108	100	2.6	310	100	0	200	4
111	100	2.6	400	100	—	250	8
112	100	2.7	320	95	—	310	4
113	100	2.6	350	88	—	330	2
114	100	2.7	300	70	—	300	2
115	100	2.7	250	50	—	270	2
118	100	2.6	300	75	—	290	6
119	100	2.7	280	60	—	270	2
120	100	2.7	260	50	—	250	2
121	100	2.6	240	50	—	175	2
122	100	2.6	200	60	—	190	2
132	100	2.4	310	140	—	290	6
133	100	2.5	210	75	—	195	4
134	100	2.7	190	75	—	170	2
135	100	2.7	190	70	—	180	2
136	100	2.6	200	65	—	190	2
139	100	2.5	250	75	0	225	6
140	100	2.6	190	60	0	190	2
141	100	2.6	160	50	0	155	2

Table XXVIII. (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
142	100	2.7	150	40	0	145	2
143	100	2.7	130	40	0	130	2
146	100	2.6	170	70	0	160	4
147	100	2.6	150	50	0	140	2
148	100	2.6	160	50	0	140	2
149	100	2.7	140	40	0	130	2
150	100	2.7	140	40	0	125	2
153	100	2.7	150	40	0	145	4
154	100	2.7	130	30	0	120	2
155	100	2.8	110	30	0	105	2
156	100	2.8	120	25	0	105	2
157	100	3.0	90	15	0	85	2
160	100	2.9	100	30	0	95	2
161	100	3.0	100	20	0	90	2
162	100	3.0	100	30	0	90	2
163	100	3.1	90	20	0	85	2
164	100	3.0	120	30	0	110	4
167	100	2.9	190	50	0	170	8
168	100	2.9	200	50	0	190	4
169	100	3.0	200	40	0	190	2
170	100	3.0	170	30	0	160	2
171	100	3.0	170	30	0	150	2
174	100	3.0	160	40	0	160	4
175	100	3.0	130	20	0	120	2
176	100	3.0	110	25	0	100	2
177	100	3.0	100	20	0	100	2
178	100	3.0	110	30	0	110	2
181	100	2.9	110	30	0	110	2
182	100	3.0	90	20	0	80	2
183	100	3.0	100	20	0	100	2

Table XXIX. Pile D: Aluminia/Silica Gel (Surface Treatment)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm*	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
1	20	10.8	—	6	—	250	40
3	100	10.4	—	11	—	220	40
4	20	9.4	—	6	—	280	10
6 †	50	8.7	—	18	—	245	10
		8.2	—	5	—	162	5
10 †	100	6.8	5	5	—	260	6
		6.5	10	5	—	180	4
11	100	6.5	10	5	—	190	5
12	50	6.5	10	5	—	180	6
13	100	6.5	—	6	—	230	8
14	100	6.5	—	11	—	260	12
17	100	6.5	—	15	—	280	15
18	100	6.5	—	39	—	190	12
19	100	6.5	—	12	—	110	8
20	100	6.3	—	25	—	100	6
21	100	6.3	—	28	—	85	5
24	100	6.5	—	15	—	85	4
		6.5	—	12	—	85	4
25	100	6.5	—	22	—	100	8
26	100	6.3	—	28	—	130	15
27	100	6.3	—	39	—	95	15
33	60	5.5	60	53	13	140	15
34	100	5.0	120	65	18	165	10
35	100	4.5	350	78	33	195	12
38	100	6.7 ‡	—	22	—	95	5
39	100	6.5	—	27	—	95	5
40	100	6.5	—	22	—	80	4
42	100	6.5	—	24	—	80	4

---

*Includes finely suspended iron hydroxide.

†On days 6 and 10, only the first and last 2 ℓ of the total wash were analyzed.

‡Erosion holes plugged with alumina/silica gel.

Table XXIX (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm*	Ferrous Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
45	100	6.5	—	20	—	70	6
46	100	6.5	—	18	—	80	4
47	100	6.5	—	18	—	70	5
48	100	6.7	—	15	—	60	4
49	100	6.7	—	15	—	60	4
52	100	6.5	—	12	—	55	5
53	100	6.3	—	12	—	47	5
54	100	6.3	—	15	—	45	5
55	100	6.3	—	12	—	45	4
56	100	6.2	—	12	—	47	5
59	100	6.2	—	15	—	55	6
60	100	6.2	—	12	—	50	4
61	100	6.2	—	12	—	50	4
62	100	6.2	—	15	—	50	4
63	100	6.2	—	15	—	55	4
66	100	6.0	—	20	—	70	6
67	100	6.1	—	12	—	60	4
68	40	6.2	—	15	—	70	6
73	100	6.1	—	20	—	85	8
74	100	6.0	—	25	—	95	8
75	100	6.0	—	30	—	110	4
77	100	6.0	—	30	—	100	4
80	100	5.6	—	55	—	330	6
81	100	5.5	—	60	—	350	4
82	100	5.5	—	66	—	375	6
83	100	5.6	—	55	—	310	4
84	100	5.5	—	70	—	330	4
87	100	5.4	—	90	—	360	6
88	100	5.5	—	66	—	380	4
89	100	5.4	—	56	—	380	4
90	100	5.4	—	56	—	330	2
91	100	5.4	—	44	—	365	4

---

* Includes finely suspended iron hydroxide.

Table XXIX (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate ppm	Soluble Silica, ppm
94	100	5.2	—	70	—	420	6
95	100	4.7	—	110	—	470	4
96	100	4.4	—	110	—	420	6
97	100	4.4	—	95	—	420	4
98	100	4.2	—	85	—	380	4
101	100	4.0	—	110	—	418	8
102	100	4.0	—	110	—	380	6
103	100	4.2	—	70	—	350	4
104	100	3.8	—	100	—	330	4
105	100	3.6	—	80	—	290	4
108	100	3.2	560	110	—	380	6
109	100	3.4	550	130	—	330	4
110	100	3.2	500	150	—	360	4
111	100	3.1	500	130	—	340	2
112	100	3.1	450	130	—	280	2
115	100	2.7	550	148	—	380	8
116	100	2.7	500	120	—	360	4
117	100	2.6	500	110	—	380	4
118	100	2.7	450	110	—	360	2
119	100	2.7	400	90	—	300	2
129	100	2.5	490	230	—	405	12
130	100	2.5	305	120	—	275	4
131	100	2.5	315	100	—	285	2
132	100	2.7	340	90	—	310	2
133	100	2.5	360	110	—	340	2
136	100	2.5	400	120	0	370	4
137	100	2.5	380	120	0	340	2
138	100	2.5	430	130	0	410	4
139	100	2.5	410	110	0	395	4
140	100	2.5	450	130	0	420	2
143	100	2.3	530	200	0	500	4
144	100	2.4	500	170	0	480	4
145	100	2.4	500	160	0	470	2

Table XXIX (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Ferrous Iron, ppm	Sulfate ppm	Soluble Silica, ppm
146	100	2.5	480	150	0	470	2
147	100	2.5	460	160	0	450	2
150	100	2.6	500	150	0	480	6
151	100	2.7	470	140	0	440	4
152	100	2.7	480	140	0	460	4
153	100	2.7	460	140	0	440	4
154	100	2.7	400	100	0	380	2
157	100	2.6	430	120	0	400	2
158	100	2.6	410	120	0	400	2
159	100	2.7	380	100	0	370	2
160	100	2.7	360	110	0	330	2
161	100	2.7	400	130	0	390	2
164	100	2.7	400	100	0	370	4
165	100	2.9	310	80	0	280	2
166	100	2.8	320	80	0	300	2
167	100	2.9	280	90	0	260	2
168	100	2.7	280	80	0	260	2
171	100	2.7	330	85	0	330	2
172	100	2.9	260	70	0	250	2
173	100	3.0	230	50	0	200	2
174	100	3.0	210	40	0	200	2
175	100	3.0	180	30	0	170	2
178	100	2.8	220	45	0	220	2
179	100	2.8	240	60	0	230	2
180	100	2.8	270	85	0	270	2

Table XXX. Pile E: Alumina/Silica Gel (In-Depth Treatment)

Day	Volume of Water, ℓ	pH	Alkalinity as $CaCO_3$, ppm*		Dissolved Iron, ppm†	Sulfate ppm	Soluble Silica, ppm
			P	M			
1‡	50	10.5	700	950	8	530	30
2	100	9.1	250	320	15	380	10
3	100	8.3	110	170	11	250	6
4	100	7.4	40	65	7	170	4
7	100	6.8	0	20	5	190	6
8	100	6.8	10	40	5	140	5
9	100	7.0	0	30	5	120	4
10	100	7.0	10	60	5	140	4
11	100	7.0	12	65	5	140	4
14	100	7.1	20	90	5	170	5
15	100	7.0	18	85	5	150	4
16	100	6.8	0	60	5	140	4
17	100	6.6	0	70	5	140	4
18	100	6.6	0	70	5	160	4
21	100	6.5	0	60	5	160	6
22	100	6.3	0	43	5	170	4
23	40	6.5	0	70	5	180	6
28	100	6.3	0	50	8	200	8
29	100	6.0	0	35	5	240	4
30	100	6.0	0	20	5	190	4
32	100	6.0	0	30	5	190	6
35	100	6.1	0	50	5	210	10
36	100	6.0	0	40	8	190	4
37	100	6.0	0	65	10	220	6
38	100	6.1	0	45	6	190	4
39	100	6.1	0	30	5	175	4
42	100	6.0	0	50	6	190	6
43	100	6.0	0	60	5	160	4

---

*P alkalinity is obtained by titrating with H_2SO_4 to the phenophthalein end point. M alkalinity is obtained by titrating with H_2SO_4 to the methyl orange end point. If 2P-M is positive, alkalinity is due to hydroxide. If M-2P is positive, alkalinity is due to bicarbonate.

†Includes finely suspended iron hydroxide.

‡This pile was violently disturbed on the first day of washing

Table XXX (Cont.)

Day	Volume of Water, ℓ	pH	Alkalinity as $CaCO_3$, ppm		Dissolved Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
			P	M			
44	100	6.0	0	40	5	100	4
45	100	6.0	0	70	5	100	2
46	100	5.9	0	30	5	95	2
49	100	6.0	0	45	5	95	4
50	100	5.9	0	40	8	110	2
51	100	6.0	0	65	8	110	4
52	100	6.0	0	65	5	95	4
53	100	6.0	0	50	5	95	6
56	100	6.0	0	80	5	130	8
57	100	6.0	0	95	5	110	4
58	100	6.0	0	70	5	100	2
59	100	6.0	0	45	5	110	2
60	100	6.0	0	55	5	95	2
63	100	6.0	0	70	10	135	2
64	100	6.0	0	55	8	120	2
65	100	6.0	0	65	8	130	2
66	100	6.0	0	60	10	100	2
67	100	6.0	0	40	10	110	2
70	100	6.0	0	70	10	130	4
71	100	6.0	0	80	8	100	4
72	100	6.0	0	65	8	95	2
73	100	6.0	0	70	5	76	2
74	100	6.0	0	90	5	90	2
84	100	6.1	0	50	8	95	10
85	100	6.0	0	60	5	80	2
86	100	6.0	0	60	5	80	4
87	100	6.2	0	80	5	90	2
88	100	6.0	0	65	5	80	2
91	100	5.8	0	40	5	90	10
92	100	6.0	0	70	5	75	6
93	100	6.0	0	50	5	85	2
94	100	6.0	0	55	5	85	2
95	100	6.0	0	70	5	70	2

Table XXX (Cont.)

Day	Volume of Water, ℓ	pH	Acidity as $CaCO_3$, ppm	Dissolved Iron, ppm	Sulfate, ppm	Soluble Silica, ppm
98	100	5.5	100	15	95	6
99	100	5.6	80	10	80	6
100	100	5.6	100	10	90	4
101	100	5.6	120	10	115	4
102	100	5.5	120	15	120	4
105	100	5.7	100	15	95	4
106	100	5.5	110	15	95	2
107	100	5.5	110	10	100	2
108	100	5.6	90	10	90	2
109	100	5.8	70	10	65	2
112	100	5.8	60	10	50	4
113	100	6.0	40	8	40	2
114	100	6.0	50	5	40	2
115	100	5.9	60	5	55	2
116	100	5.9	40	5	40	2
119	100	6.0	50	5	40	2
120	100	6.0	50	5	40	2
121	100	6.0	40	5	40	4
122	100	6.0	30	5	30	2
123	100	6.0	40	5	30	2
126	100	6.0	60	8	60	2
127	100	6.0	30	5	40	2
128	100	6.0	30	5	40	2
129	100	6.0	20	5	40	2
130	100	5.9	50	8	40	2
133	100	5.9	60	10	60	2
134	100	6.0	20	5	80	2
135	100	6.0	10	5	50	2

APPENDIX III

AMD GENERATION MECHANISM

Examination of data on Pile A in Appendix II gives some insight into the mechanism of AMD generation. It is clear that the pile generates an AMD of a highly concentrated nature, similar to that reported by other investigators. From the data taken on the first and second days, it can be seen that the inner collection area produced a more concentrated acid water than the outer area. When the conical shape of the pile is taken into consideration, this result seems reasonable, since the wash water contacted more acidic rock in the center than in the outer area and therefore should have been more concentrated.

The results of days 6 through 13 show that regular washings reduce the concentration of the AMD, but if the refuse is allowed to sit wet and unwashed for a few days, the pollutant content of the wash effluent rises again. This is dramatically verified by the data on days 16 and 23. The pile had been left for 7 days without being washed, and when the washings were resumed the resulting AMD was considerably more concentrated than at the beginning of the 7-day period.

All these observations suggest that the wet pile is slowly generating AMD and the washings are merely flushing out the previously produced oxidation products. The fact that the first 20 ℓ of wash effluent on day 23 were very concentrated while the next 100 ℓ were far more dilute tends to support this hypothesis. Yet a small scale laboratory test appears to contradict this concept which has been suggested by other investigators.

A separatory funnel was half filled with fresh coal refuse (about 250 g) and 250-ml quantities of distilled water were passed through the funnel as fast as it could drain out the bottom (about 2 min per wash). Each successive wash was started as soon as the previous one had completely drained out of the funnel. The effluent was analyzed for pH as shown in Table IX. Clearly, the acid production remained almost constant throughout this test, although the refuse was completely immersed in water during each wash. The pH appears to be slowly rising, indicating that the acid water is being washed out of the rock; yet 2 days later the pH is still at 3.9. Obviously, the concept of AMD being slowly produced and being washed out by "rain" or artificial washings is not completely satisfactory.

It had been felt that all this washing could have little effect on the composition of the remaining rock, but the calculation of the total sulfur removed from the pile proved this untrue. After 570 ℓ of water had passed through the pile, a total of 3395 g of sulfate or 1132 g of sulfur had been removed from the rock. If one assumes that the rock is about 12% sulfur, this represents 4.4% of the total sulfur in the pile.

Table XXXI. Rapid Washing of Coal Refuse

Amount of Wash Water	pH
500	3.8
750	3.3
1000	3.1
1250	3.3
1500	3.3
1750	3.3
2000	3.3
2250	3.5
2500	3.5
2750	3.7
3000*	3.3
4000†	3.9

---

* After 1 hr.

† 2 days later.

Examination of the data in Table XXXI shows that the pile is being washed at a much faster rate than could occur in the natural state. The 570 ℓ of wash water is equivalent to about 34 in. of "rain," almost a year's precipitation in 3 weeks. From the limited amount of data available, it is not clear what effect this highly accelerated test rate is having on the data.

BIBLIOGRAPHIC: **ACCESSION NO.**

Tyco Laboratories, Inc., Silicate and Alumina/Silica Gel Treatment for the Prevention of Acid Mine Drainage, Final Report FWQA Project No. 14010DLI, April 1970

ABSTRACT

A treatment technique has been demonstrated on a laboratory scale which inhibits or prevents the generation of acid mine water from waste cool refuse. Three variations of the general method were considered:

1. Neutralization of the water-accessible refuse with a dilute solution of sodium silicate (waterglass)
2. Development of a continuous gel on the refuse surface structure which sealed off the entire pile from natural runoff waters
3. Development within the pile structure of a continuous silica/alumina gel to eliminate percolation through the refuse and minimize the effect of natural erosion of the gel structure.

KEY WORDS

Silica Gel
Acid Mine Drainage
Coal Refuse
Alumina/Silica Gel
Water Pollution
Accelerated Testing
Weatherability
Neutralization
Waterglass
Gel Forming Methods

BIBLIOGRAPHIC: **ACCESSION NO.**

Tyco Laboratories, Inc., Silicate and Alumina/Silica Gel Treatment for the Prevention of Acid Mine Drainage, Final Report FWQA Project No. 14010DLI, April 1970

ABSTRACT

A treatment technique has been demonstrated on a laboratory scale which inhibits or prevents the generation of acid mine water from waste cool refuse. Three variations of the general method were considered:

1. Neutralization of the water-accessible refuse with a dilute solution of sodium silicate (waterglass)
2. Development of a continuous gel on the refuse surface structure which sealed off the entire pile from natural runoff waters
3. Development within the pile structure of a continuous silica/alumina gel to eliminate percolation through the refuse and minimize the effect of natural erosion of the gel structure.

KEY WORDS

Silica Gel
Acid Mine Drainage
Coal Refuse
Alumina/Silica Gel
Water Pollution
Accelerated Testing
Weatherability
Neutralization
Waterglass
Gel Forming Methods

BIBLIOGRAPHIC: **ACCESSION NO.**

Tyco Laboratories, Inc., Silicate and Alumina/Silica Gel Treatment for the Prevention of Acid Mine Drainage, Final Report FWQA Project No. 14010DLI, April 1970

ABSTRACT

A treatment technique has been demonstrated on a laboratory scale which inhibits or prevents the generation of acid mine water from waste cool refuse. Three variations of the general method were considered:

1. Neutralization of the water-accessible refuse with a dilute solution of sodium silicate (waterglass)
2. Development of a continuous gel on the refuse surface structure which sealed off the entire pile from natural runoff waters
3. Development within the pile structure of a continuous silica/alumina gel to eliminate percolation through the refuse and minimize the effect of natural erosion of the gel structure.

KEY WORDS

Silica Gel
Acid Mine Drainage
Coal Refuse
Alumina/Silica Gel
Water Pollution
Accelerated Testing
Weatherability
Neutralization
Waterglass
Gel Forming Methods

ABSTRACT (Cont.)

Comparison of the effluent water with an untreated pile shows the neutralized pile was effective for a minimum of 120 in. of equivalent rainfall in inhibiting AMD generation. The surface gel was effective for a longer period of time. The most effective treatment utilized a mixed alumina/silica gel formed within the pile at depths up to 6 in. This method was effective for more than 500 in. of equivalent rainfall, the duration of the test, and appeared to be exceptionally stable at that time.

The weathering resistance of the treatment methods was evaluated by heating the gel treated refuse in the laboratory and exposing it to rain, snow, and freeze-thaw cycles outdoors. Extensive washings of the weathered test materials established the fact that the treatments were effective for at least 120 in. of equivalent rainfall (the duration of the test) in preventing AMD generation.

This report was submitted in fulfillment of Contract No. 14-12-500 between the Federal Water Quality Administration and Tyco Laboratories, Inc.

ABSTRACT (Cont.)

Comparison of the effluent water with an untreated pile shows the neutralized pile was effective for a minimum of 120 in. of equivalent rainfall in inhibiting AMD generation. The surface gel was effective for a longer period of time. The most effective treatment utilized a mixed alumina/silica gel formed within the pile at depths up to 6 in. This method was effective for more than 500 in. of equivalent rainfall, the duration of the test, and appeared to be exceptionally stable at that time.

The weathering resistance of the treatment methods was evaluated by heating the gel treated refuse in the laboratory and exposing it to rain, snow, and freeze-thaw cycles outdoors. Extensive washings of the weathered test materials established the fact that the treatments were effective for at least 120 in. of equivalent rainfall (the duration of the test) in preventing AMD generation.

This report was submitted in fulfillment of Contract No. 14-12-500 between the Federal Water Quality Administration and Tyco Laboratories, Inc.

ABSTRACT (Cont.)

Comparison of the effluent water with an untreated pile shows the neutralized pile was effective for a minimum of 120 in. of equivalent rainfall in inhibiting AMD generation. The surface gel was effective for a longer period of time. The most effective treatment utilized a mixed alumina/silica gel formed within the pile at depths up to 6 in. This method was effective for more than 500 in. of equivalent rainfall, the duration of the test, and appeared to be exceptionally stable at that time.

The weathering resistance of the treatment methods was evaluated by heating the gel treated refuse in the laboratory and exposing it to rain, snow, and freeze-thaw cycles outdoors. Extensive washings of the weathered test materials established the fact that the treatments were effective for at least 120 in. of equivalent rainfall (the duration of the test) in preventing AMD generation.

This report was submitted in fulfillment of Contract No. 14-12-500 between the Federal Water Quality Administration and Tyco Laboratories, Inc.